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HgCdTe FABRICATION USING DIRECTED ENERGY TECHNIQUES

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The goal of this research was to produce large-area, thin-film single-crystal HgCdTe material for infrared detectors. Single-crystal CdTe films were deposited by heteroepitaxial evaporation on muscovite mica substrates, and subsequently converted to single-crystal $Hg_{(1-x)}Cd_{(x)}Te$ by vapor exchange at a constant temperature. These films had excellent stoichiometry, uniform composition, and good electrical properties; however, the films were not useful on the mica substrates nor were they successfully transferred to other substrates. Attempts at depositing single-crystal CdTe films on sapphire,

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BaF_2, zirconia, and quartz were unsuccessful. Attempts to grow single-crystal CdTe films on sapphire by liquid-phase epitaxy using pulsed electron beams to melt thin deposited films were also unsuccessful. It is believed that the goals of this program could be met by a different evaporation furnace design which would allow in situ cleaning of the substrate surface.

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FOREWORD

The work reported in this document was performed in part at Spire Corporation, Bedford, Massachusetts, and in part at New England Research Center, Inc., Sudbury, Massachusetts, under contract MDA 903-81-C-0410, DARPA Order Number 3800. The contract monitor was Mr. Sven Roosild.

The program manager at Spire was Dr. Robert Wolfson. The principal investigator at Spire was Dr. Anton Greenwald, who was in charge of pulsed electron beam processing. The program manager at NERC was Dr. Theodore Wong. The project engineer at NERC was Dr. Robert Martineau, and the task engineer was Mr. Chris Devaney, who was in charge of the epitaxial deposition and vapor exchange processes.

The report of the subcontractor, NERC, is included in Section 2. Work performed at Spire Corporation is described in Section 3.

SUMMARY

The goal of this work was to produce thin single-crystal films of $Hg_{1-x}Cd_xTe$ at least 2 inches in diameter for use in infrared detectors.

Single-crystal films of CdTe were deposited on one inch diameter mica substrates by the hot wall epitaxy (HWE) method. This process was reproducible. However, a change in substrate materials was mandated as mica was not suitable for the final devices and the completed film was not successfully transferred. A new furnace was constructed for the HWE process to handle large samples with improved temperature control. In this furnace large diameter (2 inches) films of CdTe were grown on sapphire substrates of various orientations, but the films were not single-crystal. Experiments with other suitable materials also yielded polycrystalline films. It is believed that, with improvements in the furnace design, single-crystal films could be produced which would yield detector grade $Hg_{1-x}Cd_xTe$.

Existing films of CdTe on mica were converted to single-crystal $Hg_{1-x}Cd_xTe$ by evaporation and diffusion at constant temperature (EDICT). Good control of thickness, composition, uniformity, and reproducibility was demonstrated for 0.5 inch square samples. The electron mobility of these films was measured as $1.5 \times 10^5 cm^2/V-s$ at $77^\circ K$. The structure of polycrystalline CdTe films on sapphire was not significantly improved by the EDICT process.

The surface morphology of these CdTe and HgCdTe films was improved by pulsed electron beam polishing. This is a process which rapidly melts a thin surfical layer of the target material; rapid cooling (≤ 1 usec) prevents loss of stoichiometry. Two micron thick, polycrystalline CdTe films were also melted on sapphire substrates but did not exhibit liquid phase expitaxial regrowth as expected. Co-evaporated films of Hg and Te on single crystal CdTe wafers were pulse melted and also did not show epitaxial regrowth.

SECTION 1
INTRODUCTION

1.1 OBJECTIVE

The overall purpose of this program was to grow large, single crystal HgCdTe material suitable for use in large scale infrared detector arrays. The following material parameters were design goals for this program:

- Compositional uniformity with $\Delta x < 0.0006$
- Heteroepitaxial single crystal films, 2 inch diameter
- Net foreign impurity concentration $< 5 \times 10^{14}$ atom/cm^3

The original program objective also included the demonstration that the process developed was capable of producing crystals with the aforementioned properties in sufficient quantities to be able to meet the future needs of DOD through the 1980's.

1.2 TECHNICAL CONSIDERATIONS

Existing melt growth methods of fabricating HgCdTe crystals are unsatisfactory for two reasons. First, the high vapor pressure of Hg at the melt temperature of HgCdTe of the desired composition limits the size of the ampoule in which the material may be grown. Second, the wide separation of the liquidus and solidus in the pseudobinary phase diagram makes it very difficult to achieve uniform composition across large specimens.

This program was a continuation of research begun under contract number MDA903-79-C-0434 (DARPA order number 3800) which sought a thin film solution to the problems discussed above. Results of the first phase of this program are summarized below:

- Heteroepitaxial single crystal films of CdTe one inch in diameter were grown using a Hot Wall Epitaxy (HWE) technique on cleaved mica substrates.

- Single crystal HgCdTe films over 1cm^2 were produced by a subsequent EDICT (Evaporation and Diffusion at Constant Temperature) treatment of the CdTe films.

- The variation in compositional uniformity over $1cm^2$ was less than 0.0007 in the value of x for $Hg_{1-x}Cd_xTe$.

- High electron mobility, $1.5 \times 10^5 cm^2$/volt-sec at 77^oK, in this material indicated epitaxial film quality comparable to that in bulk material.

- Pulsed electron beam polishing of the surface of CdTe was demonstrated. The feasibility of directed energy processing of HgCdTe was demonstrated.

- The feasibility of pulsed diffusion of Hg films on initially cold (77^oK) CdTe substrates was demonstrated.

The current phase of this program demonstrated the reproducibility of this process. An increase in the size of the sample films on a more appropriate substrate was sought in this phase of the program. Additional goals were to reduce the contamination of this material, improve the surface finish, and maintain the uniformity achieved.

This program was terminated early. Thin films with the required properties were produced by an alternate technique, molecular beam epitaxy. It is still believed that the methods of fabricating such films investigated here are feasible, but that there was insufficient time to resolve difficult technical problems.

1.3   GENERAL METHODS

The method used in this program achieved the desired end of large area, uniform single-crystal HgCdTe films in two steps. The first step is to grow heteroepitaxialy large single-crystal films of CdTe on foreign substrates by the Hot Wall Epitaxy (HWE) technique. This is an evaporation type process. The second step is transformation from single-crystal CdTe film to single crystal HgCdTe film by a process of vapor growth and solid state diffusion known as EDICT (Evaporation and Diffusion at Constant Temperature).

This two-step method has a number of advantages over other methods of growing large area HgCdTe single-crystal specimens. First, the film thickness is determined by the deposition of CdTe in the initial step, whereas the critical Hg-Cd ratio is determined by the second step. This process allows critical parameters to be separately optimized. Second, since all processes take place at relatively low temperatures, the excessive mercury pressure that plagues most high-temperature melt-growth processes is not a problem. In fact, this method takes advantage of the volatility of the components and grows from the vapor phase. Scaling up of the specimen dimensions is rather straightforward relative to melt-growth methods, which are all limited by the 1/2 inch ampoule dimension as a result of high mercury pressures. Third, segregation problems which limit the uniformity of composition in melt-grown HgCdTe do not exist in this method, because melting of the bulk material is not required here. Futhermore, since HgCdTe is grown directly in a thin CdTe film, no compositional gradient occurs. Thus, exceptionally uniform composition should result both across and normal to the film surface. Finally, both the HWE and EDICT processes are vapor-growth methods where the emphasis is placed on the growth of epitaxial layers under conditions as near as possible to thermodynamic equilibrium, resulting in thin films of bulk quality and crystalline perfection.

An additional processing step is necessary to produce a smooth surface. The growth morphology of the as-deposited CdTe film after HWE is faceted, with surface relief greater than one micron. The surface features after EDICT conversion to HgCdTe show many spiral growth terraces. How the surface morphology of the HgCdTe film relates to that of the original CdTe sample is not yet known. Polishing a thin film is difficult and costly. However, rapid melt and quenching by irradiation with a pulsed electron beam produces a superior surface finish. As the surface cools after melt, epitaxial crystal growth prevents degradation of the structure. The short time at high termperature, less than one microsecond, minimized diffusion of the volatile components. The process is fast, noncontaminating, inexpensive, and amenable to large scale manufacture.

Liquid-phase expitaxial crystal growth after rapid melting by a pulsed electron beam was also investigated as a method for producing CdTe and HgCdTe films. Thin polycrystalline CdTe films deposited on sapphire by HWE were melted by pulsed heating. These films remained intact after cooling, but did not show an improvement in crystal structure. In another experiment thin films of Hg and Te were co-evaporated onto a single-crystal substrate of CdTe cooled to 77°K. The film was pulse heated in situ by an electron beam; after processing the film had a polycrystalline structure. The reason for failure of this approach to give heteroepitaxial growth is not known; homoepitaxial crystal growth has been observed for other materials systems.

SECTION 2
REPORT OF SUBCONTRACTOR NERC

2.1 HOT WALL EPITAXY

2.1.1 Process Description

The first step in the process for obtaining HgCdTe was the epitaxial growth of thin CdTe films, about 10 um thick, on suitable substrates. The technique employed for the vapor deposition process is knows as Hot Wall Epitaxy (HWE). In essence, the HWE process involves thermal evaporation of a pure CdTe source in a hot-walled airtight enclosure and subsequent epitaxial growth of CdTe on a heated foreign substrate.

Several factors must be considered in any vapor growth process involving CdTe. First, CdTe evaporates according to the reaction:

$$CdTe(s) \rightarrow Cd(g) + 1/2 \ Te_2(g) \tag{1}$$
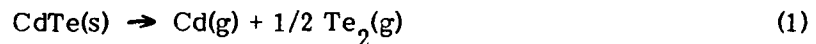
The component partial pressures of Cd and Te_2 vapors are not necessarily equivalent and in fact, for a stoichiometric CdTe source, they differ by an order of magnitude at typical sublimation temperatures; Cd being the greater at 10^{-3} torr. Hence, stoichiometry of the deposit must be considered. Secondly, CdTe is known to grow in several different polymorphic forms, the two most commonly observed being the cubic (sphalerite) and hexagonal (wurtzite) forms. Thus, controlled nucleation must be maintained as well.

In the HWE process a source of stoichiometric CdTe is maintained at a temperature T_2 in an airtight enclosure (the HWE growth chamber) and the substrate is maintained at a slightly lower temperature T_1. The temperature differential $T_2-T_1 = T$ is maintained by independent control of the source and substrate temperature. The enclosure walls are also heated at T_2 to preserve stoichiometry.

Source evaporation proceeds according to the decomposition reaction (1). Vapor transport occurs in response to the temperature gradient ΔT and results in vapor saturation near the substrate at temperature T_1. By adjusting the overall magnitude of the temperature differential, the nucleation and growth rates can be controlled to yield high-quality, single-crystal films with minimum defects.

In the HWE process, the overall stoichiometry of the grown film is preserved even in light of gross component partial pressure differences because (1) the deposition takes place in an airtight enclosure under near equilibrium partial pressures; (2) deposition rates are maintained at reasonably low levels so that desorption and reaction takes place slowly on the surface of the growing film; and (3) substrate temperature is maintained high enough to enhance surface diffusion which promotes stoichiometric balance.

2.1.2 HWE Apparatus

The vacuum system for this apparatus consists of a 400 l/s turbomolecular pump backed by a mechanical fore pump. Through overnight pumping, pressures in the 10^{-8} torr range can be achieved in the process chamber. The vacuum vessel attached to the pump without a gate valve is a 10-inch diameter pyrex belljar incorporating a liquid nitrogen trap. The support for the belljar contains eight high-vacuum feedthroughs for power, sensors, and a mechanical shutter to operate the furnace.

The initial two-zone HWE quartz furnace is shown in Figure 2-1a mounted inside the belljar with heat shields in place and is shown in Figure 2-1b with the components separated. Modifications were made to this furnace to more closely approximate a gas tight enclosure (Figure 2-2). These modifications involved changes in the thermocouple location and attachment techniques, substrate holder, supporting envelope design and removal of the shutter. Sixteen CdTe films were grown on cleaned mica substrates in calibrating this sytem, demonstrating reproducibility, and in providing samples for optimization of the EDICT process discussed in Section 2.2.

(a)

(b)

S81028P
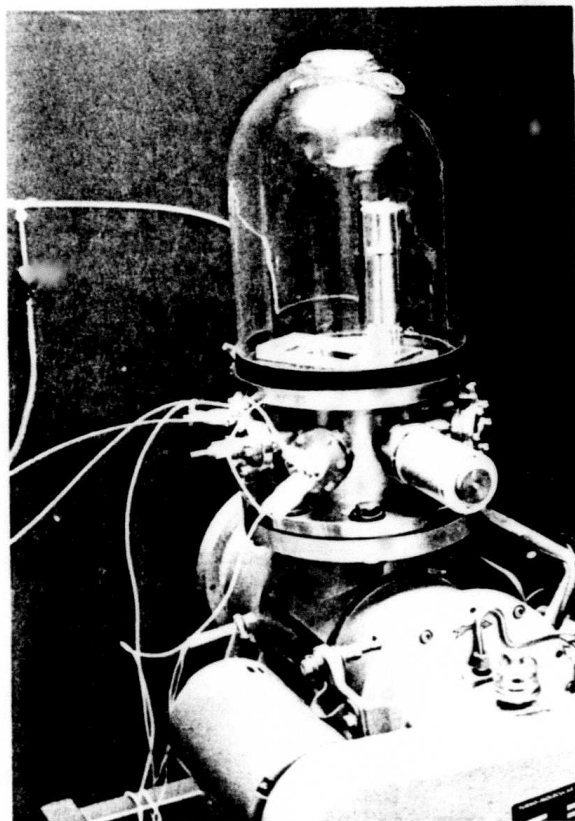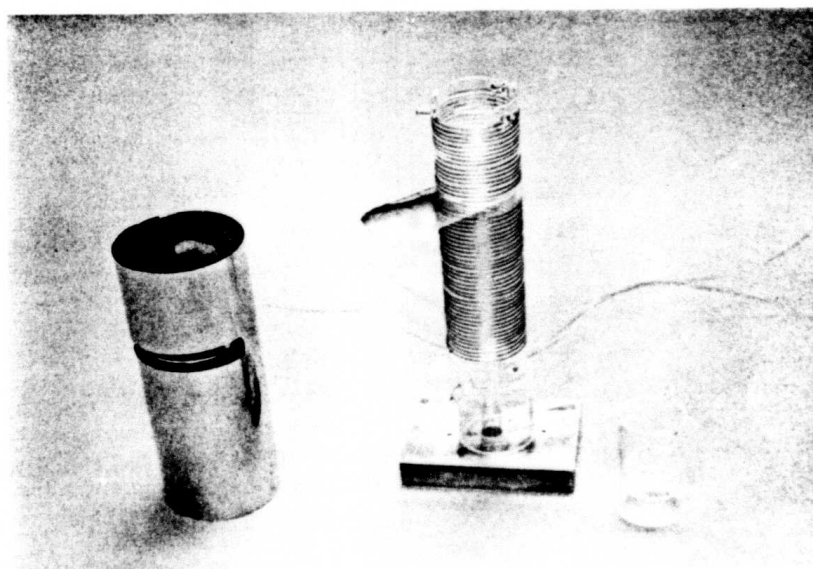
FIGURE 2-1   APPARATUS FOR THE DEPOSITION OF CdTe FILMS:
(a) Furnace Mounted in Bell Jar on Vacuum Pump
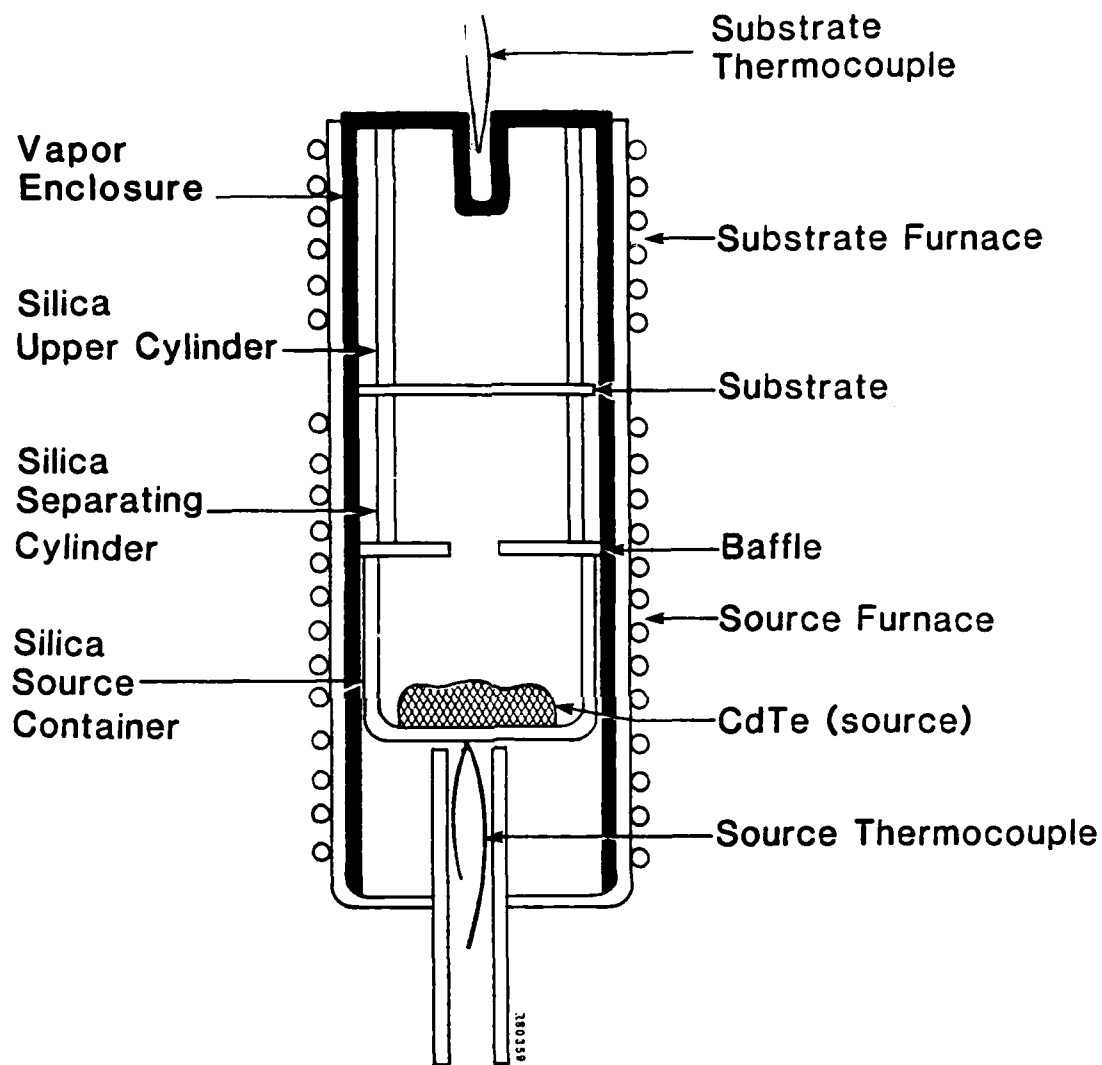(b) Detail of Furnace with Shutter and Heat Shield

FIGURE 2-2. HOT WALL FURNACE WITH ENCLOSED SOURCE FOR
EVAPORATION OF CdTe

It had become evident from this earlier work that the lack of control over process parameters such as source to substrate temperature differential, growth time, and the inability to maintain quasi-equilibrium conditions within the growth enclosure seriously limited our ability to produce single crystal CdTe thick films with reproducible properties on any foreign substrate except mica. Since the existence region for single crystal growth (the relationship between source and substrate temperature) for CdTe on basal plane mica substrates is quite broad (see Figure 2-3), it was possible to produce single crystal films routinely within minimal control over process variables. However, on other substrates such as BaF_2 and sapphire, CdTe has a much narrower single crystal existence region, and it was necessary to provide control and stability of process parameters over much narrower limits.

During the latter part of this program a new HWE system was designed. Besides providing for a greater substrate area (2 inch diameter films), it had improved thermal control. A schematic diagram of the last iteration on furnace design is shown in Figure 2-4. See references (1) and (2) for further details.

2.1.3 Experimental Results, HWE on Mica

Mica substrates for this program were prepared by cleaving high quality mineralogical muscovite. This material cleaves on the (0001) basal plane. The substrates were used as-cleaved without further preparation.

Films grown during this phase of the program varied in thickness from 8 to 15 um. The deposition rate was a function of both source and substrate temperatures. In a series of runs where the source temperature was constant, i.e. the same vapor flux of cadmium and tellurium, it was found that the growth rate increased with substrate temperature. The growth rate data for a source temperature of $490^{\circ}K$ is plotted in Figure 2-5. This same data shown on an Arrhenius plot in Figure 2-6 yielded an activation energy of about 4 kcal/mole. Activation energies of this order of magnitude indicate a diffusion mechanism as the rate-controlling step and is typical of many vapor phase depositions.
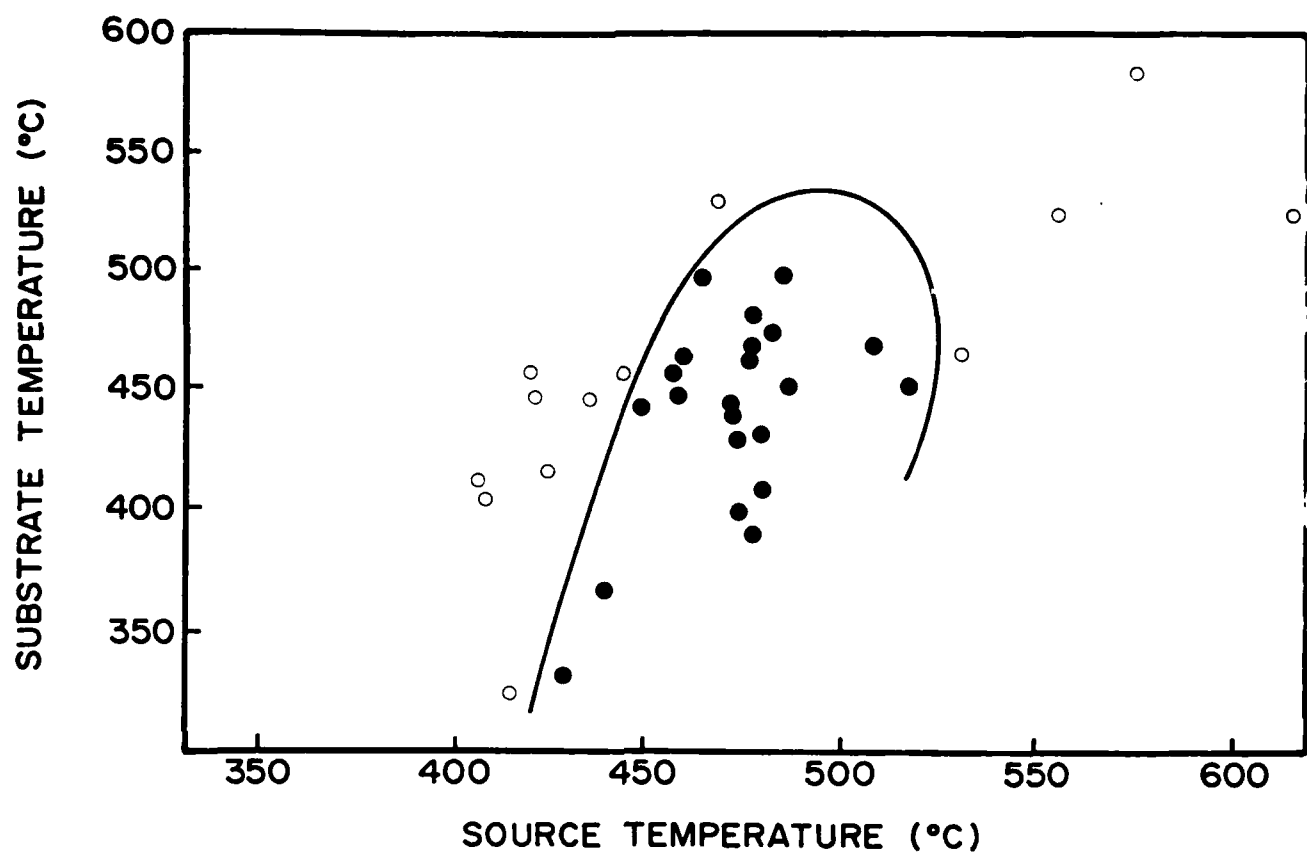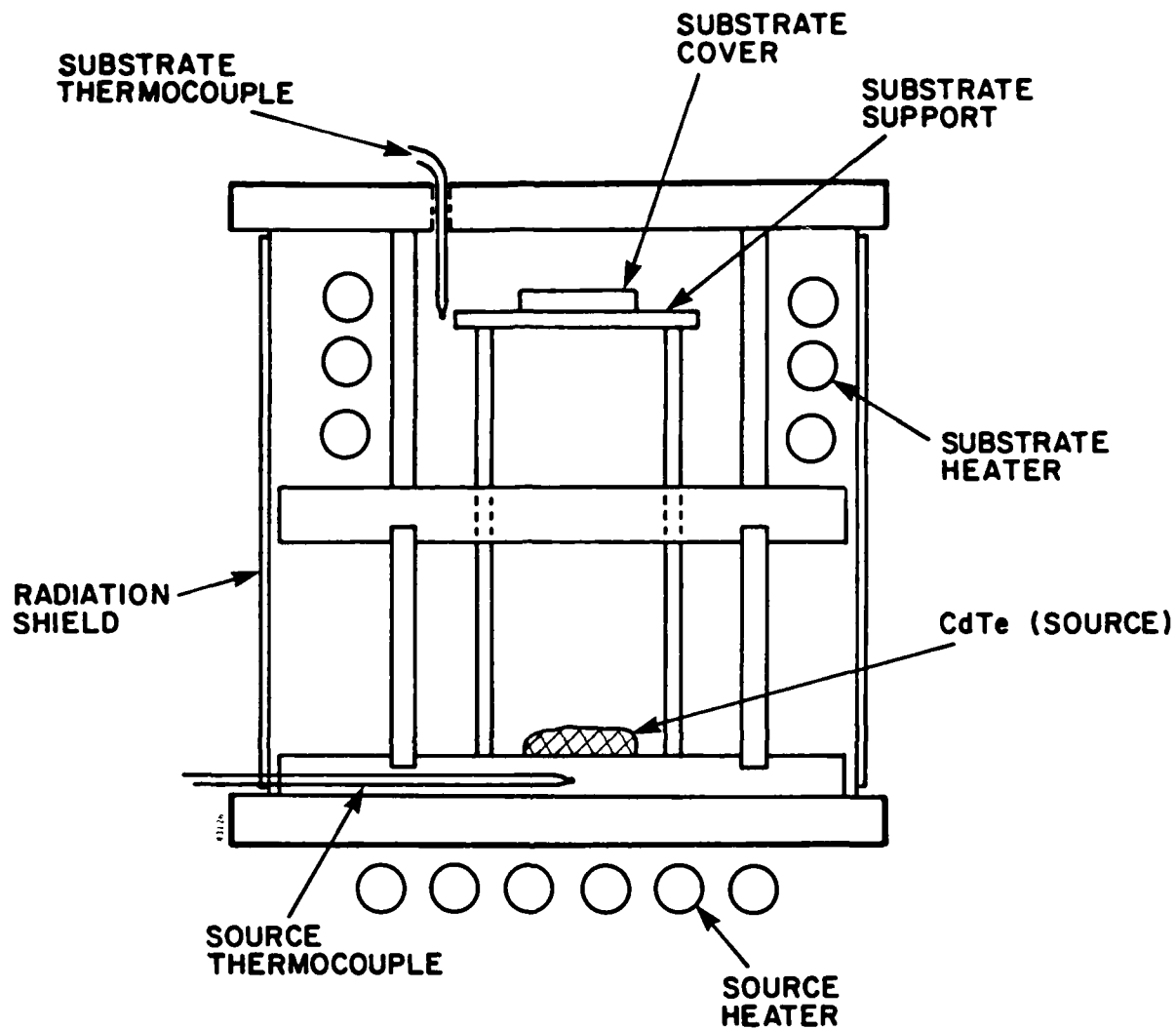
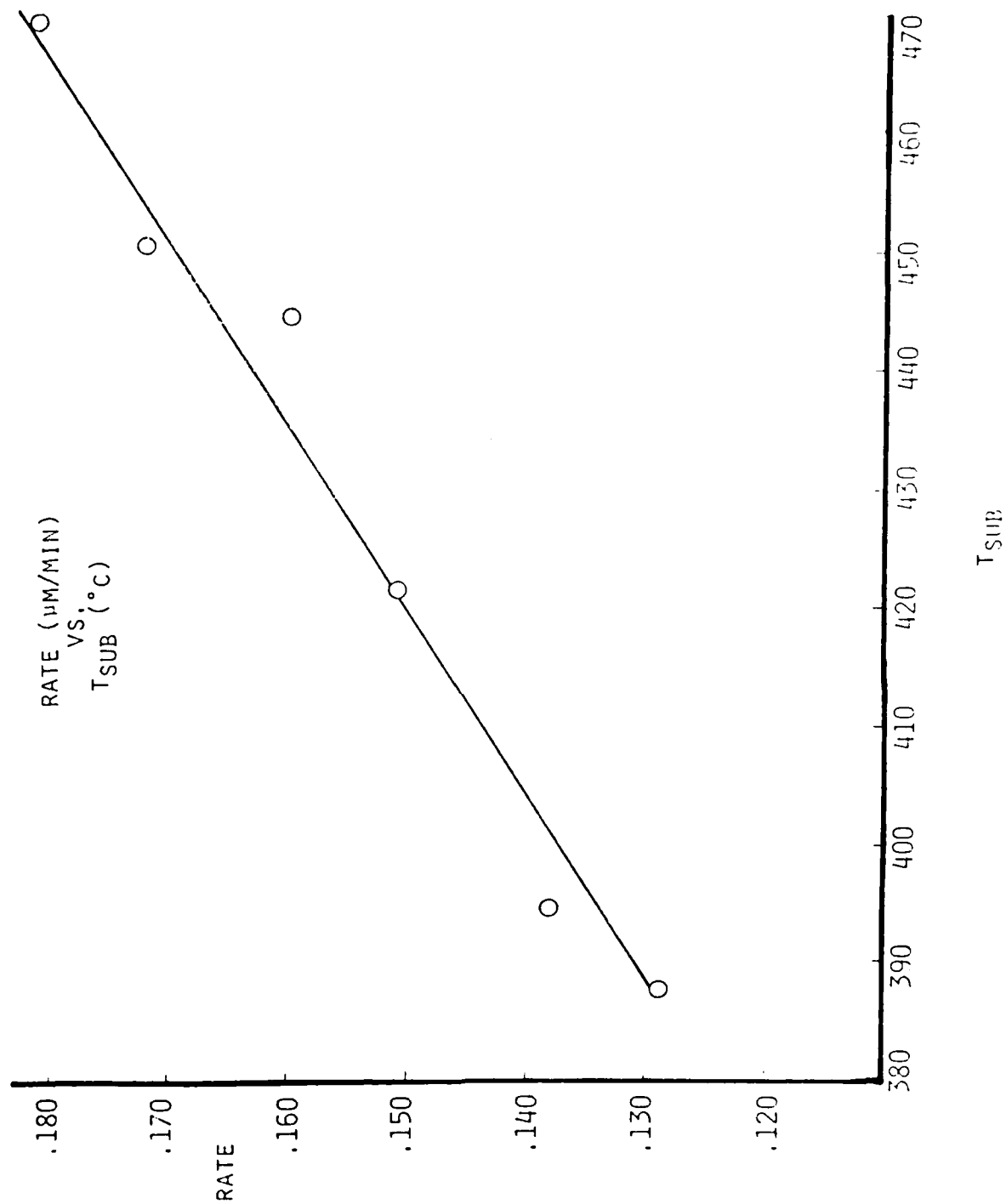FIGURE 2-3   CdTe ON MICA EXISTENCE REGION

FIGURE 2-4.   HWE FURNACE

RATE (μM/MIN)
VS.
T_{SUB} (°C)

T_{SUB}

FIGURE 2-5.   DEPOSITION RATE OF CdTe ON MICA AS A
FUNCTION OF SUBSTRATE TEMP   TU

2-8

LOG R (µM/MIN)
VS.
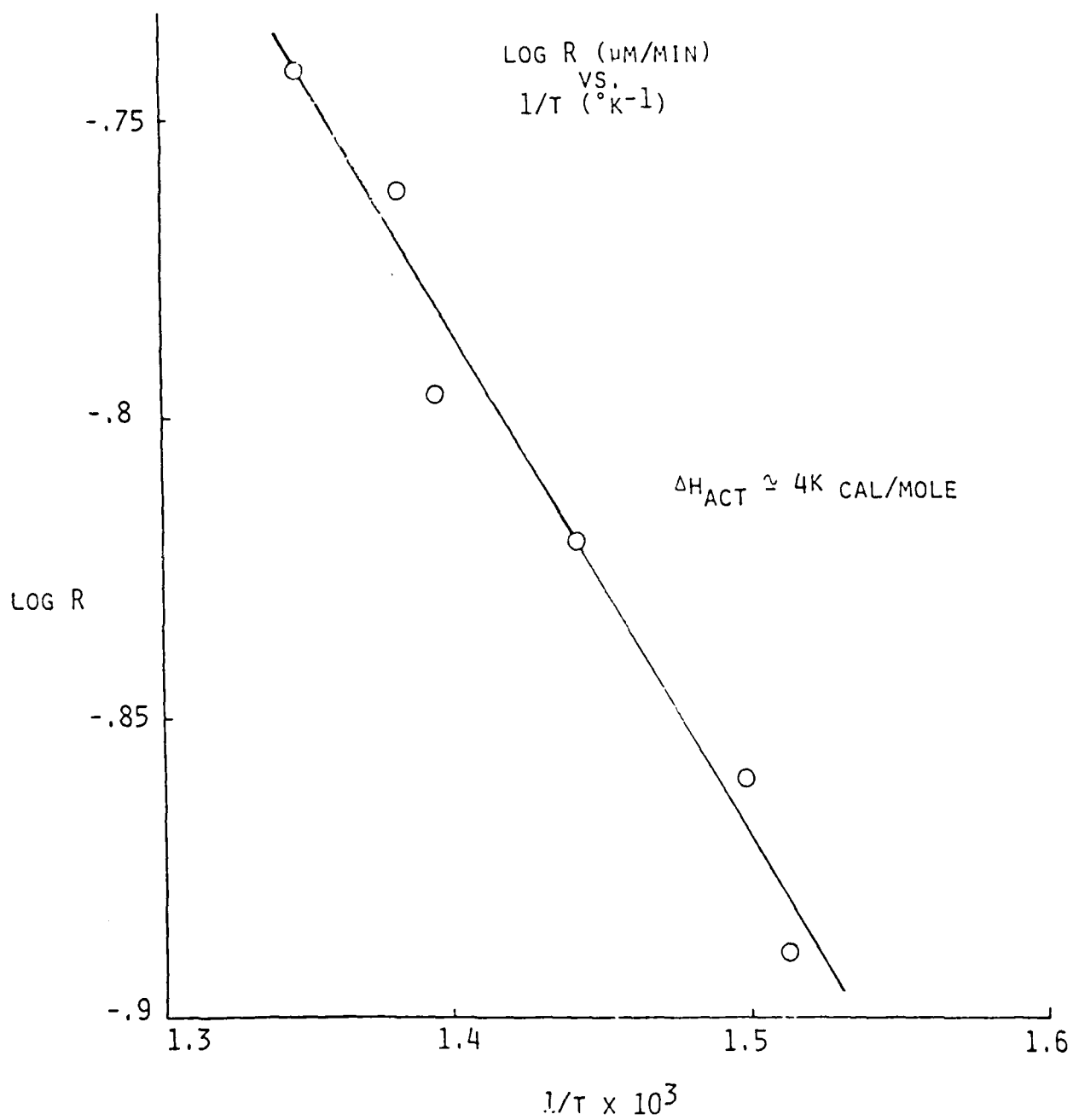1/T (°K-1)

$\Delta H_{ACT} \simeq 4K$ CAL/MOLE

FIGURE 2-6.   LOG OF CdTe DEPOSITION RATE (R) ON MICA
AS A FUNCTION OF INVERSE SUBSTRATE
TEMPERATURE (T).

Back reflection Laue x-ray patterns were used to analyze CdTe films on mica. The results were similar to those obtained in the first phase of this program. This work was performed using Cu x-rays from a 20 keV, 2 mA electron beam source with a 2 hour exposure. An example of a pattern is shown in Figure 2-7. Comparison of similar patterns with CdTe films to patterns from mica alone show additional x-ray spots presumably due to the CdTe. The pattern from CdTe films on mica showed six-fold symmetry with clear spots, indicating epitaxial growth of a single crystal film. The orientation of the film is (111), which corresponds to the basal plane (c axis) of the mica substrate.

Photographs of two CdTe films deposited on mica substrates under optimized growth conditions are shown in Figure 2-8. The scale is in inches showing the present size of CdTe crystals routinely grown by the HWE process. The surfaces of these films are dull, with a rough texture seen in the microphotograph of Figure 2-9. This surface morphology is related to the crystal structure and might be improved with a change in substrate.

2.1.4 Experimental Results, HWE on Sapphire Substrate Preparation

All sapphire substrates were thin disks, up to 2 inches in diameter, cut and polished from single crystal boules. Three orientations were selected for investigation: perpendicular to the C axis (0001), parallel to the C axis (1120), and (1102) which is the standard silicon-on-sapphire orientation. Surface etching and cleaning was required prior to deposition. The cleaning procedure used involved initial degreasing, surface etching, and final solvent vapor cleansing. The initial degreasing removes any grease or oils resulting from wafer handling as well as remnant grit from the polishing stage through light abrasion with powdered detergent under running deionized wafer. Sapphire etching is performed next by immersing the wafer in hot electronic grade phosphoric acid for five to fifteen minutes. This removes surface atoms but at a very slow rate; hence, the need for long etch times. After several deionized water rinses the wafer is propped on a quartz stand in a sealed beaker of boiling propanol so that the wafer is entirely above the liquid. Propanol vapor condenses, rolls down the substrate and returns to the liquid. This vapor cycle action is allowed to continue for thirty to forty-five minutes after which the wafer is removed, dried, and placed in the HWE system for deposition.
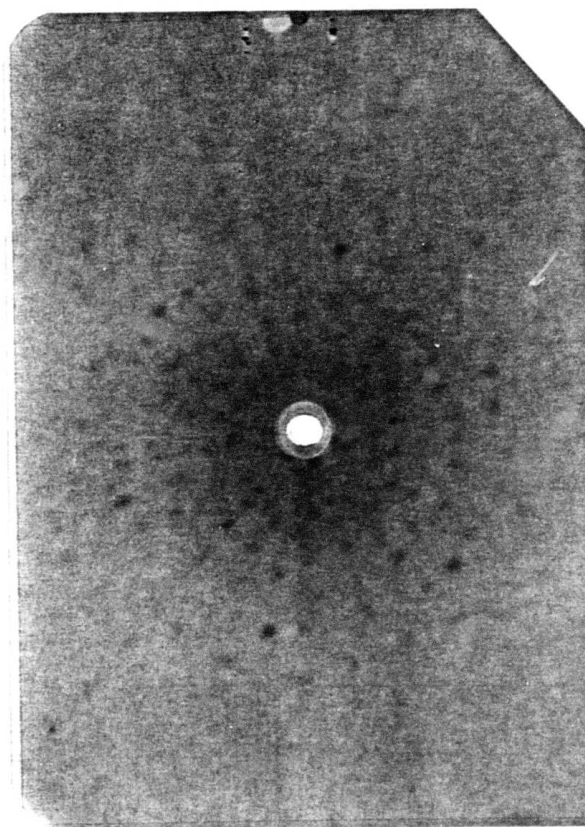
(a)

FIGURE 2-7   BACK-REFLECTION LAUE PATTERN FROM CdTe FILM ON
MUSCOVITE MICA (SPECIMEN M81). Pattern as recorded,
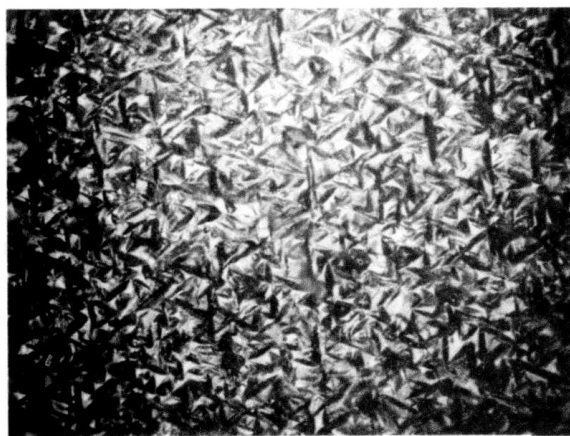negative image; molybdenum radiation, 20 kV/20 mA, 5 h exposure.
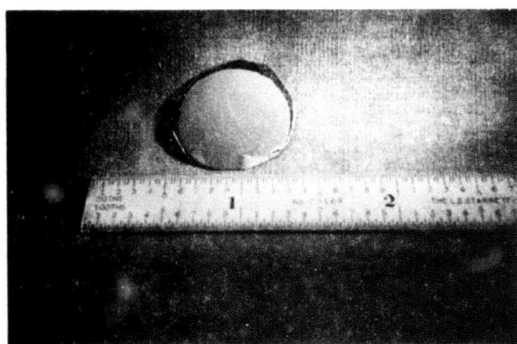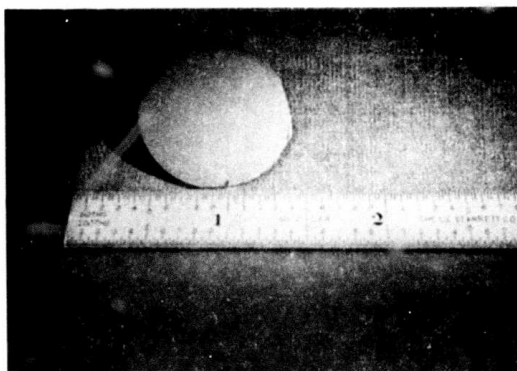
FIGURE 2-8.   HWE GROWN CdTe on MICA

20 μm

FIGURE 2-9.   MICROPHOTOGRAPHS OF HWE GROWN CdTe/MICA
SHOWING SURFACE STRUCTURE

Film Growth

CdTe films were grown on sapphire substrates in the improved HWE furnace described in section 2-2. Different substrate and source temperatures were used, but all such films were polycrystalline. It was found that the growth rate of the CdTe films was dependent upon the sapphire substrate temperature, similar to the case for mica. This relationship is shown in Figure 2-10 when the source temperature was held at $500^{\circ}C$. Figure 2-11 shows the Arrhenius plot of this data from which an activation energy of 47 kcal/mole was derived. Activation energies of this nature are for bonding rather than diffusion limited processes. It may be that the number of nucleation sites is so far greater on these polycrystalline films than on a single crystal film that bond formation became the deposition rate limiting step.

A strong (111) texture is evident for films grown above a source temperature of $475^{\circ}C$. The degree of texture and the crystallite size increased with source temperature, as shown in Figure 2-12 at $500^{\circ}C$ compared to Figure 2-13 at $600^{\circ}C$. The largest single crystal regions were about 0.7mm long and appeared as mirror-like plates embedded in a polycrystalline matrix. A typical embedded single crystal is shown in Figure 2-14.

Besides varying the source and substrates temperatures, the difference between the two (ΔT) was varied from $10^{\circ}C$ to over $100^{\circ}C$. The best films were those with (111) texture. Average grain size from ΔT greater than $100^{\circ}C$ was 100um.

Figure 2-15 shows the grain size in CdTe films grown under identical thermal conditions for the three different substrate orientations. The grain size increases slightly as the substrate orientation approaches the C axis. That is:

$$G_{(1120)} < G_{(1102)} < G_{(0001)}$$

where G is the grain size.

The mechanical properties of the CdTe on sapphire are far superior to those on mica substrates. Adhesion is much improved even after several thermal cycles from room temperature to $77^{\circ}K$ and no evidence of film spalling or flexing has been found.
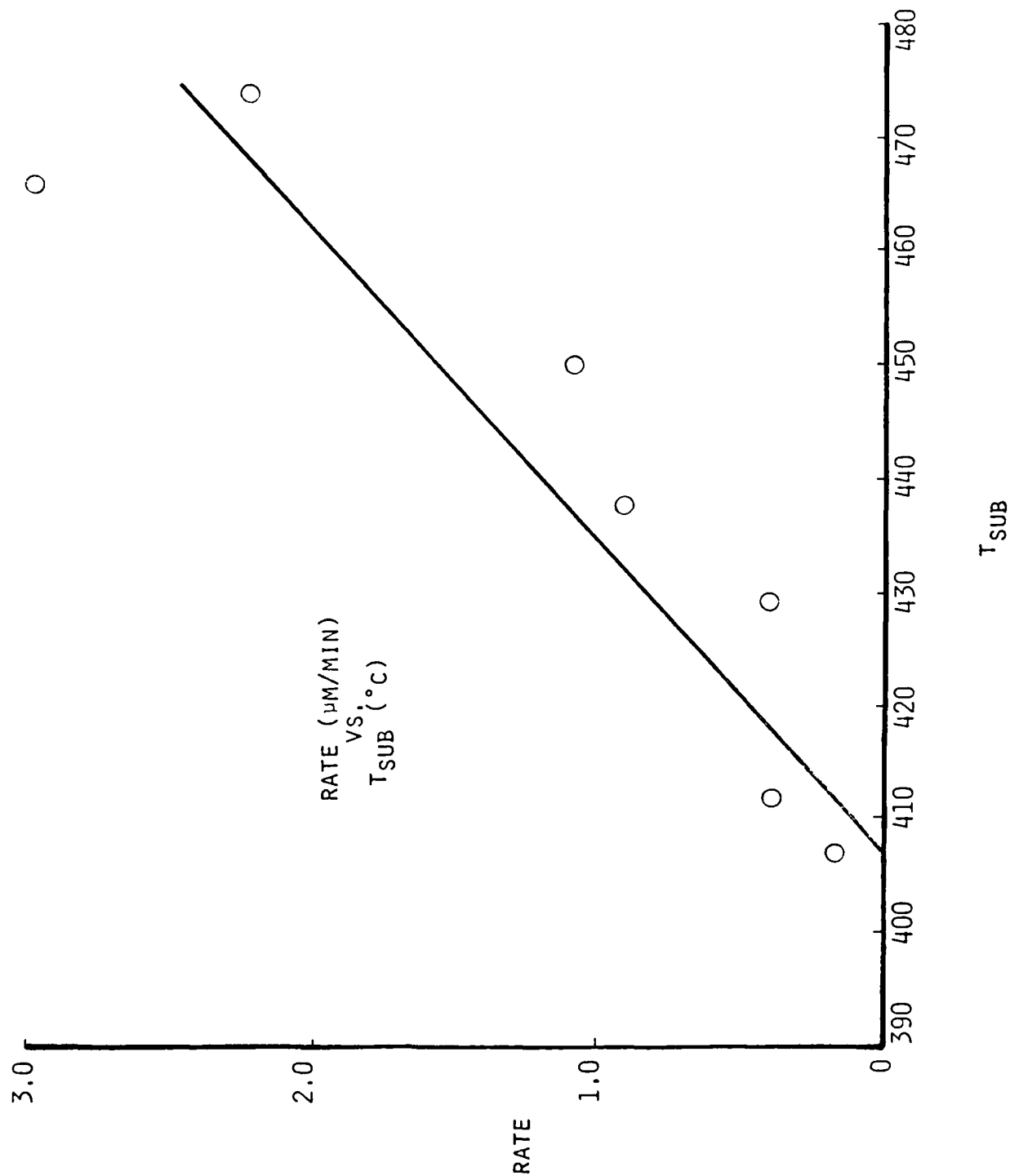
RATE (μM/MIN)
VS.
T_{SUB} (°C)

T_{SUB}

FIGURE 2-10. DEPOSITION RATE OF CdTe AS A FUNCTION OF
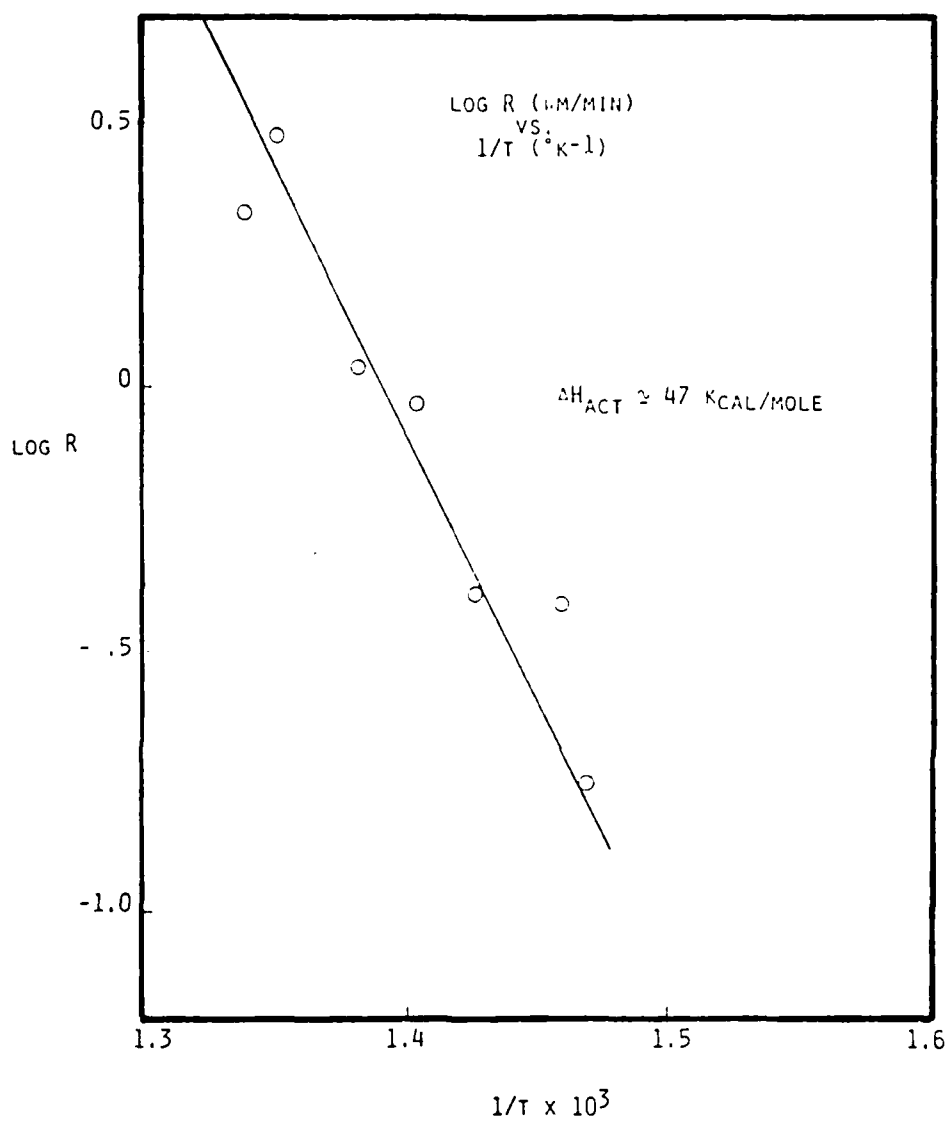SAPPHIRE SUBSTRATE TEMPERATURE FOR A SOURCE
TEMPERATURE OF 500ºC.

FIGURE 2-11. ARRHENIUS PLOT OF DEPOSITION RATE R OF CdTe
AS A FUNCTION OF SAPPHIRE SUBSTRATE TEMPERATURE
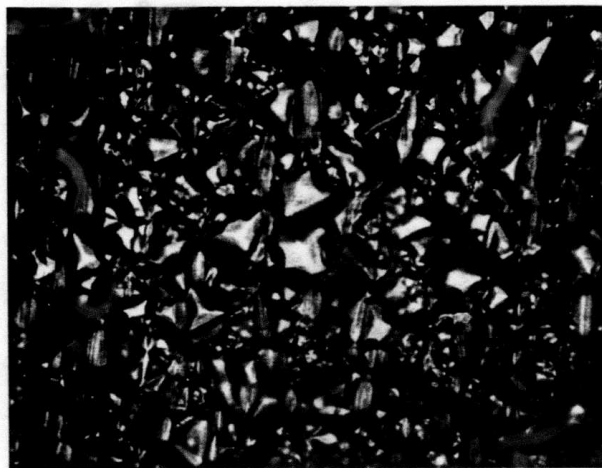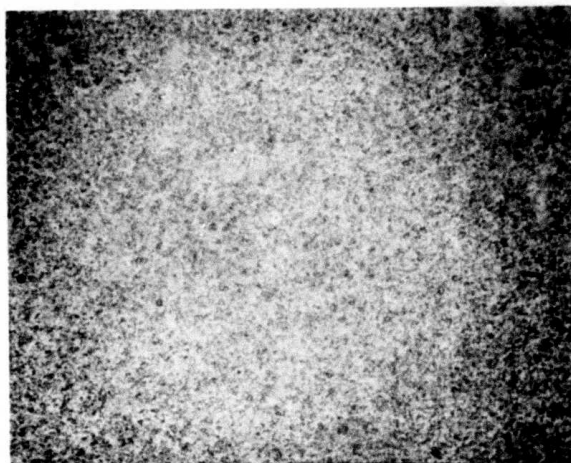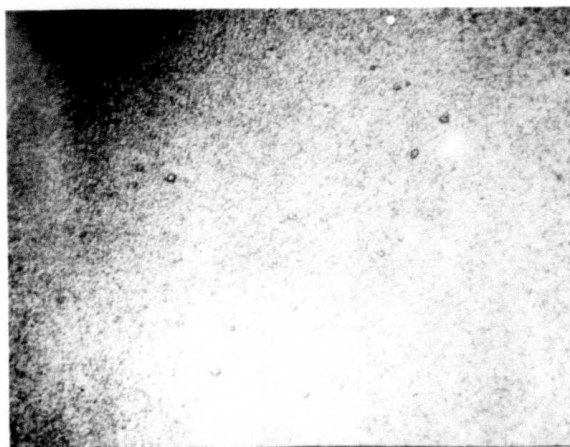T FOR A SOURCE TEMPERATURE OF 500oC.

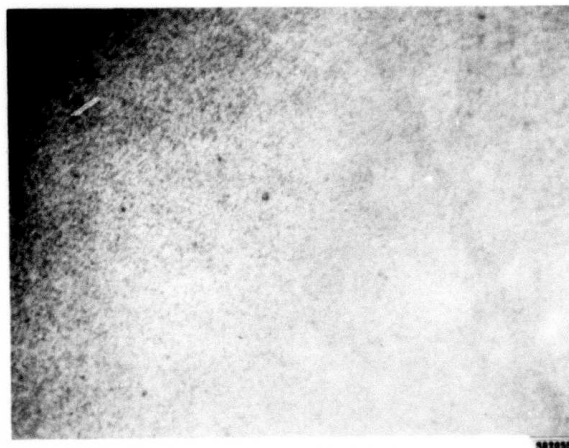FIGURE 2-12. (111) TEXTURED CdTe ON SAPPHIRE GROWN AT
$T_{source} = 500^{o}C$ (380X)

FIGURE 2-13.   (111)TEXTURED CdTe ON SAPPHIRE GROWN AT
$T_{source} = 600^{o}C$ (380X)
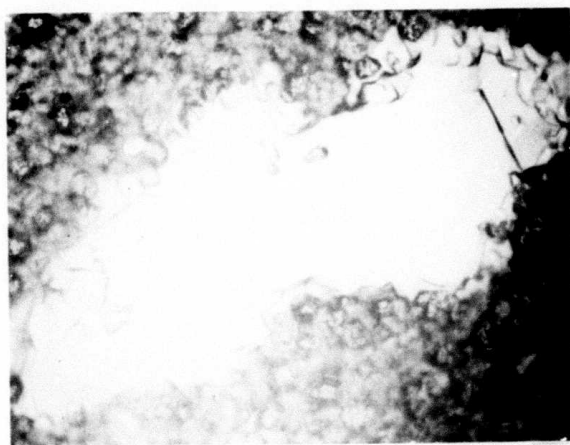
Plane Perpendicular
to C axis

Plane at 45° to
C axis

Plane parallel to
C axis

FIGURE 2-14.   STRUCTURE COARSENING DUE TO ORIENTATION.
Growth parameters are: source temperature 450°C,
substrate temperature 325°C, growth time 90 minutes

2-19

500 µm

FIGURE 2-15. SINGLE CRYSTAL CdTe EMBEDDED IN POLYCRYSTALLINE MATRIX

2.1.5 Experimental Results, HWE on Other Substrates

Besides mica and sapphire, other substrate materials were considered for HWE deposition of CdTe films. Two deposition runs were performed on each of the following materials: barium fluoride (BaF_2), stabilized cubic zirconia (ZrO_2), and fused quartz (SiO_2). Barium fluoride was tested because it has a cleavage plane which allows easy preparation of clean surfaces; however, only polycrystalline films of CdTe were deposited on BaF_2. Structural and chemical compatibility were reasons for testing zirconia, but CdTe films deposted on these substrates were also polycrystalline. Films deposited on fused quartz had large grain structure and were of poor quality compared to films deposited on mica.

### 2.2 EDICT PROCESS

2.2.1 Process Decription

The conversion of a CdTe film into single crystal $Hg_{1-x}Cd_xTe$ of controlled x value is performed using the EDICT process (Evaporation and Diffusion at Constant Temperature). This process involves the vapor transport of a precise quantity of HgTe onto the CdTe film and the homogenization of the film by isothermal diffusion.

The EDICT process requires a substrate, a source, and a control medium to be enclosed together in an evacuated ampoule. After filling and evacuation, the glass outer tube is crimped for a seal, and inserted into an isothermal furnace with careful temperature control (Figure 2-16). Total process time typically is less than 200 hours.

The substrate is a CdTe film epitaxially deposited on a foreign substrate and very carefully weighed. The source is an amount of purified HgTe calculated to be just sufficient to change the CdTe film into $Hg_{1-x}Cd_xTe$ for a given x (in this example x = .416). The weight of the control medium, a small drop of mercury, is calculated using an ideal gas approximation to be that which will give the required overpressure of mercury at the isothermal reaction temperature used. (The internal volume of the ampoule must be know in advance.)
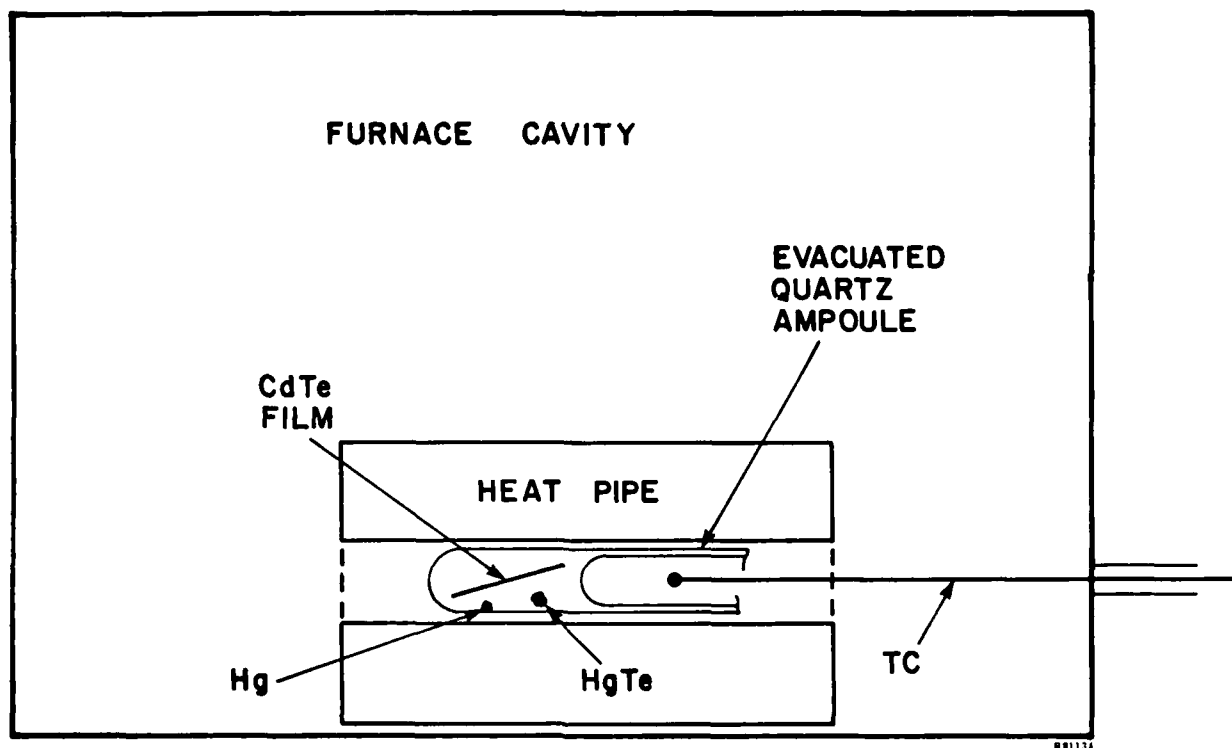
(a) General Schematic
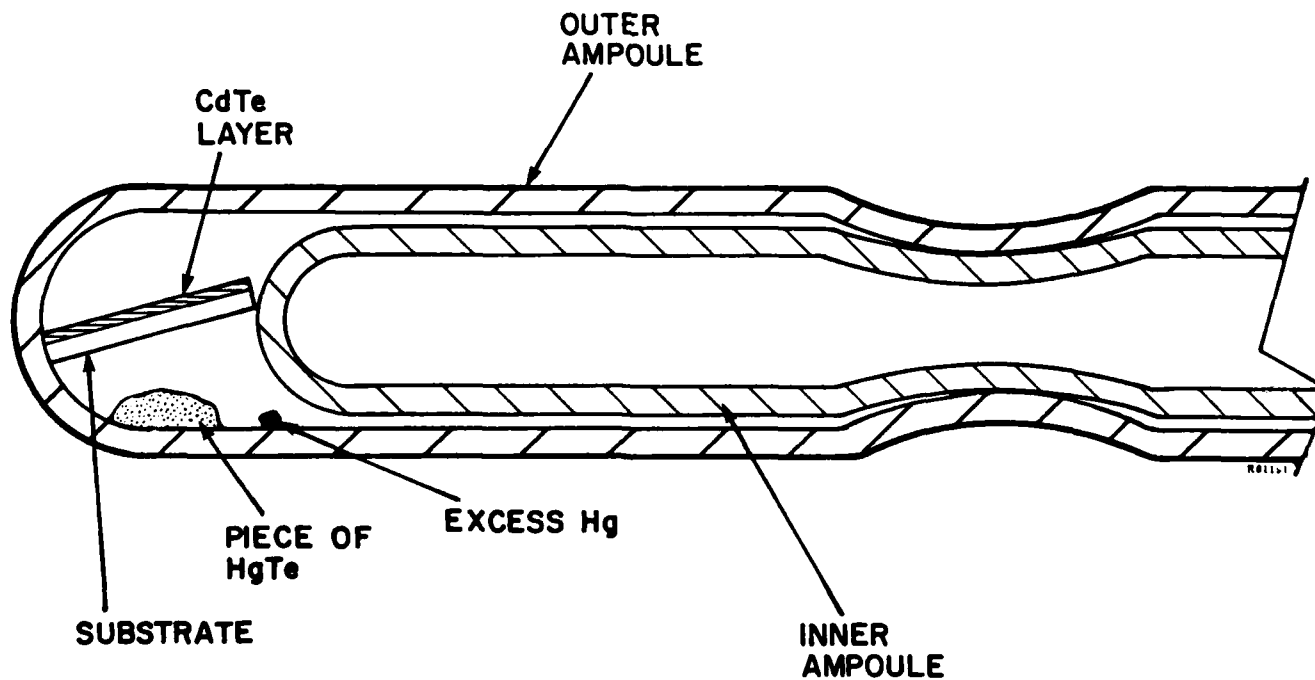
(b) Detail of Ampoule

FIGURE 2-16. EXPERIMENTAL SETUP FOR THIN FILM EDICT TRANSFORMATION

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The reaction mechanism is driven by the equilibrium pressure of the three elements (Hg, Cd, and Te) in the ampoule. This does not imply that equilibirium exists in the ampoule. Equilibrium does not exist until the reaction is complete, but the equilibrium vapor pressures indicate the way in which the reaction will proceed. In this example, the process temperature is assumed to be $830^\circ K$. The vapor pressure of mercury, cadium, and tellurium in equilibrium with the components of the ampoule at $830^\circ K$ is given in Table 2-1.

TABLE 2-1
ELEMENTAL EQUILIBRIUM VAPOR PRESSURES
AT $830^\circ K$ (atmospheres)

	Hg	Cd	Te
Hg Liquid	15.1	0	0
HgTe Solid	4.9	0	8×10^{-3}
$Hg_{.584}Cd_{.416}Te$	1.28	1.1×10^{-7}	2.3×10^{-4}

Now consider what occurs as the temperature of the ampoule is raised from $298^\circ K$ (room temperature) to $830^\circ K$. If the amount of mercury added in liquid form to the ampoule is sufficient to give an excess pressure of 0.5 atmospheres at $830^\circ K$, the CdTe surface will be bombarded by mercury atoms at a pressure of between 0.5 and 4.9 atmospheres. The former pressure is that calculated due to the excess added mercury, and the later figure is the vapor pressure of Hg over HgTe at $803^\circ K$. Because the quantity of HgTe in the ampoule is quite small (on the order of milligrams), even if it were completely evaporated it would not raise the mercury pressure to 4.9 atmospheres. The overpressure of mercury on the CdTe film will therefore be near 0.5 atmospheres. A small amount of mercury will initially be evaporated from the HgTe leaving a surface of excess Te, so that the vapor pressure of Hg over the HgTe source will also fall toward 0.5 atmospheres.

The surface of the CdTe, being bombarded by Hg, wil be covered with a mobile layer of absorbed mercury which cannot react for reasons of stoichiometry. The HgTe will be covered by a partial layer of excess Te, which will reduce the equilibrium mercury pressure over the HgTe to a value close to that determined by the excess mercury added (0.5 atmospheres in this example). The situation is a quasi-equilibrium one, and no growth occurs if the other atomic species are ignored.

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Now consider the motion of Te in the EDICT process. The vapor pressure of Te over the HgTe source will be between that of HgTe at 830°K (2×10^{-3} atm) and that of the excess Te on the surface of HgTe (8×10^{-3} atm) which results from the evaporation of mercury. The vapor pressure of Te over $Hg_{.584}Cd_{.416}$ at 830°K is 2.3×10^{-4} atm. Therefore, even after completion of the reaction, there is a chemical driving force for transfer of Te through sublimation from the HgTe source to the HgCdTe substrate due to the difference of equilibrium Te vapor pressure. Molecules of Te_2 proceed by gaseous diffusion from the source to the substrate, where they can be adsorbed on the surface and react with the excess mercury. The tellurium chemically bonds the mercury to the substrate, resulting in physical growth of the film epitaxially. Bonded mercury atoms diffuse into the substrate under the Cd-Hg concentration gradient. Capture of tellurium molecules on the surface continues until all of the HgTe source has been transferred to the substrate. Inter-diffusion of Hg and Cd continues until a uniform depth distribution for x has been achieved. Since the substrate is a thin film, inter-diffusion will be completed in a reasonably short time at the typical process temperature (830°K).

Gaseous diffusion of Cd from the substrate to the HgTe source can be neglected because the equilibrium partial pressure of Cd (Table 3-1) over $Hg_{.584}Cd_{.416}Te$ is very small compared to the pressure of tellurium or mercury. Because the molecular concentrations in the gas in the ampoule at any given temperature are proportional to the partial pressure of that component, the amount of Cd in the vapor phase is less than 10^{-6} that of Hg.

The reaction rate, or the rate of vapor growth of the HgCdTe film, is controlled by the difference in the partial pressure of tellurium over the source (HgTe) compared to the pressure over the HgCdTe substrate. The pressure of Te_2 in equilibrium with the source is affected by the excess mercury pressure. If the pressure of Hg exceeds the equilibrium vapor pressure of mercury over HgTe, then evaporation of mercury from the surface of the source will cease. In this case the vapor pressure of Te will drop because the surface of the source is no longer enriched with Te. With sufficient mercury pressure, the pressure of Te will fall to the equilibrium value over the substrate, and the reaction will stop without the driving force.

Previously published data on the isothermal growth of HgCdTe have come from experiments on bulk samples. Parameters are quite different for thin film specimens in EDICT. As previously mentioned, the limited weight of the HgTe source in EDICT limits the Hg pressure to a value close to that due to the excess liquid mercury initially admitted to the ampoule. In the bulk case, a considerable build-up of mercury pressure occurs from the available bulk of HgTe, and tellurium saturation does not occur in the gas phase. Hence, the reaction parameters of mercury pressure, reaction temperature, etc., had to be determined again under the new boundary conditions of a finite HgTe source.

2.2.2 EDICT of Films on Mica

Some of the CdTe films deposited on mica substrates, Section 2.1.3, were converted to HgCdTe by the EDICT process. Microscopic examination revealed much smoother surfaces after EDICT (Figure 2-17). Laue back reflection, x-ray diffraction indicated that the single-crystal quality of the films improved after EDICT.[3] This was demonstrated by a sharpening of the reflection spots and elimination of hazy areas in the x-ray films. Films with x=0.2 and 0.3 were easily grown.

Many difficulties with mica substrates were discovered during the course of this EDICT conversion. At the higher temperatures (over $500^{\circ}C$) used in this process, the films reacted with impurities in the mica as well as the decomposition products of mica itself. This process also seemed to increase the tendency for the film to spall from the substrate. As a consequence of this poor film adhesion and the reaction of HgCdTe on the mica, the use of mica as a supporting substrate for HWE was terminated.

2.2.3 EDICT of CdTe Films on Sapphire

EDICT runs were performed with four samples of CdTe films on sapphire. Growth parameters and results are given in Table 2-2.
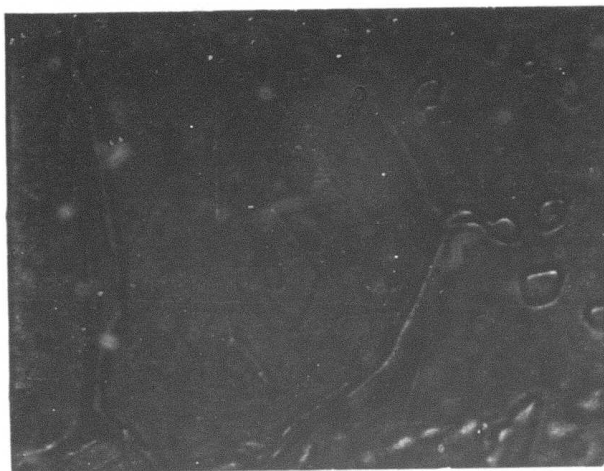
FIGURE 2-17. SINGLE CRYSTAL HgCdTe FILM ON MICA (380x)

TABLE 2-2.

GROWTH PARAMETERS AND RESULTS FROM

FOUR CdTe ON SAPPHIRE EDICT RUNS

Film	Pressure of Excess Hg (atm)	Edict Temperature (^{o}C)	Growth Time (hrs)	Loaded x Value	Final x Value After EDICT
78	.25	490	48	.200	.998
80	.25	550	88	.300	.310*
89	.25	500	24	.300	.252*
96	.25	500	72	.300	.328

*x-valued determined from FTS transmission data

Film 78 was one of the first CdTe on sapphire films grown and used a low quality CdTe source. The CdTe in this film outgassed during EDICT causing the total pressure within the sealed ampoule to rise above that of the excess Hg. This results in a termination of the vapor exchange process as explained in Section 2.2. All EDICT films on sapphire except 78 showed an enlargement in grain structure after EDICT. This phenomena is assumed to be due to the incorporation of HgTe into the CdTe film rather than recrystallization since the 78 film which had little or no HgTe exchange during EDICT did not coarsen even after a 48-hour EDICT heat treatment. Figure 2-18 is a pair of micrographs taken at 380 magnification revealing the structure coarsening due to the EDICT process. Photograph A is the CdTe on sapphire film before EDICT while B is the same film after a 72-hour EDICT heat treatment. The composition of this film after EDICT was x=.328 based on the weight increase from the HgTe incorporation. Figure 2-19 shows a similar run (80) with coarsening from an 88-hour EDICT treatment. The composition (x=.258) was measured using a Fourier Transform Spectrometer (FTS) transmission scan performed on the sample. The transmission data for both sapphire (a) and HgCdTe on sapphire (b) is shown in Figure 2-20. This film initially was a 2 um thick polycrystalline CdTe deposit on (1102) sapphire. The desired x value was .200. The actual composition as determined from the IR transmission is x=.258. The "double cutoff" curve for the HgCdTe sample is a combination of absorption from the HgCdTe which has a
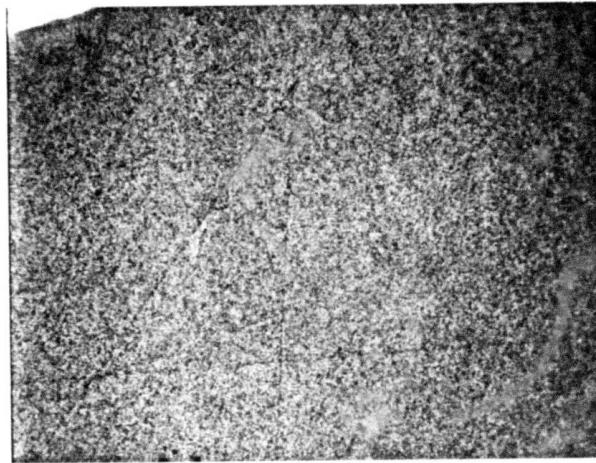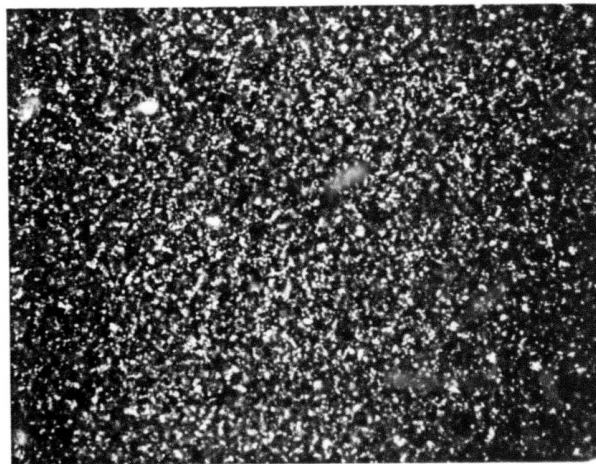
2-27
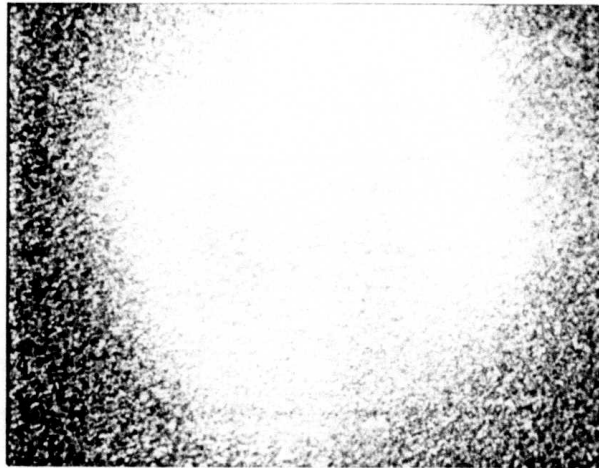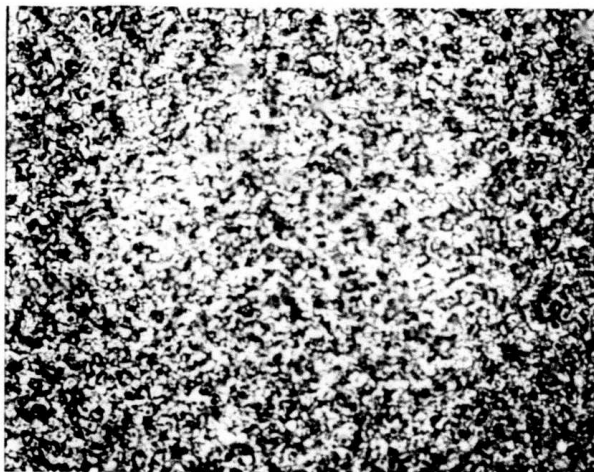
Before EDICT

After EDICT

FIGURE 2-18. GRAIN COARSENING AFTER 72 HOUR EDICT
HEAT TREATMENT (380x-Sample 96).

Before EDICT

After EDICT

FIGURE 2-19. GRAIN COARSENING AFTER 88 HOURS EDICT
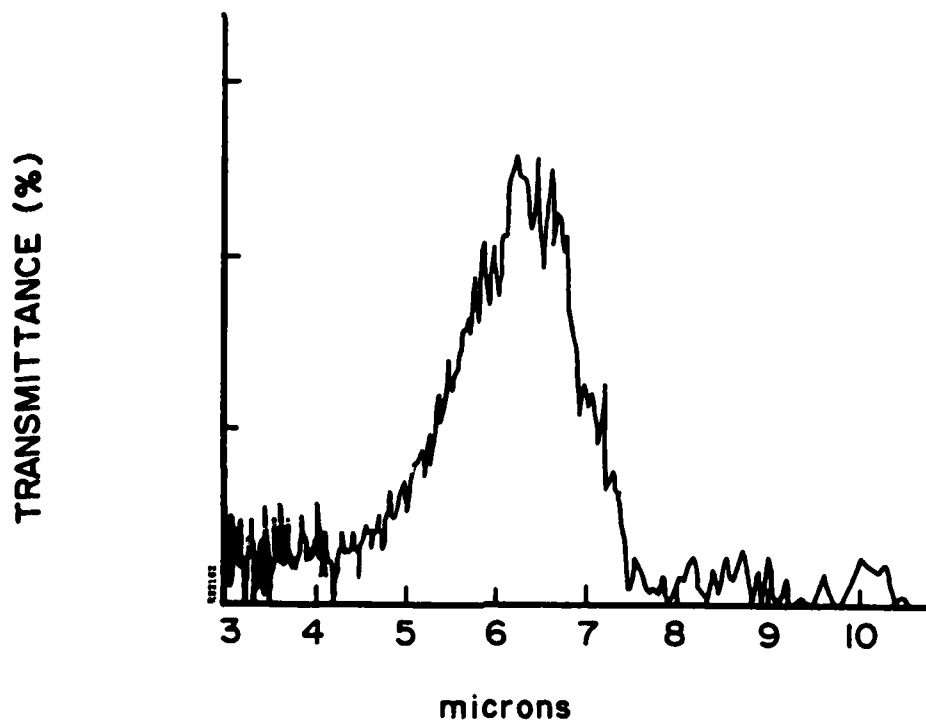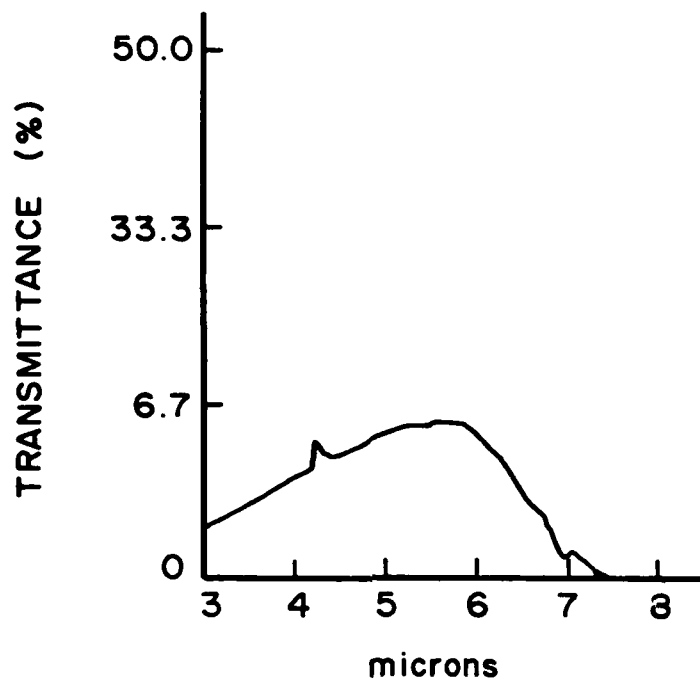HEAT TREATMENT (380x – Sample 80)

FIGURE 2-20.   TRANSMISSION CURVES FOR SAPPHIRE (top) AND
HgCdTe ON SAPPHIRE (Bottom)

300°K 50% cutoff at 5.2 um and the sapphire substrate which cuts off at 6.6 um. The FTS transmission scan is a quick way to measure composition in samples whose x value is greater than .23. For samples where x is less than .23, there is no transmission due to absorption from the sapphire substrate.

A Laue back reflection x-ray diffraction pattern of one of these HgCdTe films on sapphire is shown in Figure 2-21. The average grain size is small enough to diffract the x-rays much the same way as a powdered crystal specimen. The resulting ring structure is clearly evident, superimposed on the pattern created by the single crystal sapphire substrate. Similar ring patterns were obtained for all of the CdTe films on sapphire.

One EDICT film (80) was fabricated into PC detectors using standard photolithographic processing techniques, however, high resistance prevented any meaningful data to be collected. The high resistance was probably because the sample was so thin (~5 um after EDICT).

2.3 CONCLUSIONS AND RECOMMENDATIONS

The ability to deposit single-crystal films of CdTe up to one inch in diameter on mica substrates was clearly demonstrated under this program. These films were converted to $Hg_{1-x}Cd_xTe$ by an evaporation and diffusion process at constant temperature (EDICT) with $0.2 < x < 0.3$. Unfortunately, decomposition of the mica proved to be a problem and sapphire was then used as the substrate material. The furnace was rebuilt to accommodate two-inch substrates. CdTe films of two-inch diameter were grown on variously oriented sapphire substrates. These films, though not single crystal, were converted to $Hg_{1-x}Cd_xTe$ by the EDICT process. The resistivities of these films were too high for meaningful detector data to be measured.

During the course of the latter stages of this work, it became clear that substrate surface preparation and cleanliness were critical to obtaining high quality single-crystal films. Attempts to "bake-out" or heat treat the substrates at a temperature higher than would be used for the film growth caused preliminary vaporization of the source. Also the crystal growths on sapphire indicated that it would be necessary to slow the growth rate in order to improve the film quality.
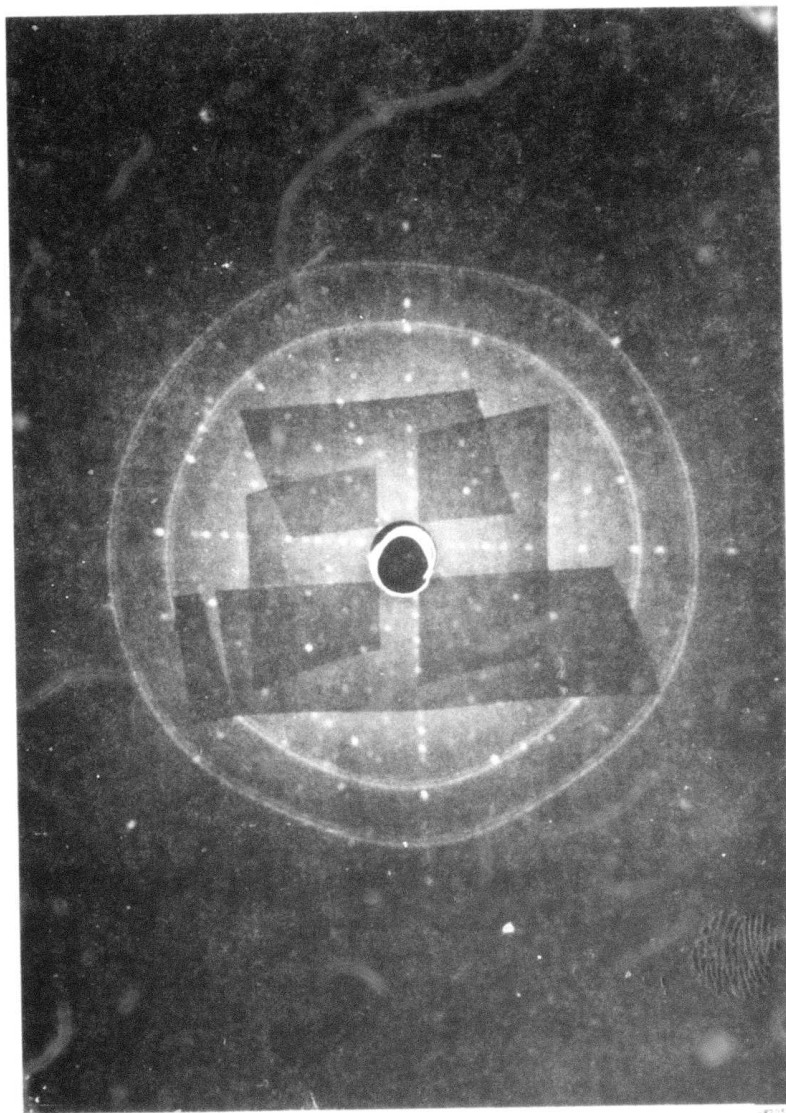
2-31

FIGURE 2-21.   BACK REFLECTION LAUE X-RAY DIFFRACTION
              PATTERN FROM POLYCRYSTALLINE HgCdTe FILM ON
              A SINGLE CRYSTAL SAPPHIRE SUBSTRATE

As a consequence of these conclusions of the film growth on sapphire, a new furnace design is recommended. This furnace should be constructed such that a high temperature "bake-out" of the substrate could be made prior to deposition of the CdTe film. Second, the furnace should be designed to provide a lower ΔT so that the film growth rate could be reduced. Finally, the furnace should be capable of reaching higher substrate temperatures to increase the surface reactivity and atom mobility. A substrate pre-heat procedure, slower growth rate and high deposition temperature should produce single-crystal films of CdTe on sapphire.

Incorporation of these modifications would result, with a high degree of confidence, in detector grade $Hg_{1-x}Cd_xTe$ on sapphire.

SECTION 3
REPORT OF THE MAIN CONTRACTOR – SPIRE CORPORATION

3.1 PULSED ELECTRON BEAM PROCESSING OF HETEROEPITAXIAL FILMS

In this context, only the CdTe films deposited on mica were single–crystal, heteroepitaxial samples. CdTe films on sapphire were all polycrystalline and are discussed in the next section (3.2) on polycrystalline and amorphous films.

3.1.1 Objective

The goal of this part of the program was to improve the characteristics of the final HgCdTe film through one of three techniques: (a) smooth the surface of the final HgCdTe film; (b) smooth the surface of the initial CdTe film; and (c) improve the crystal structure of the CdTe film. Crystal defects and the surface morphology of the as–deposited films on mica were discussed in Section 2.1. While the EDICT process (Section 2.2) did improve both the structure and morphology, the final results were not entirely satisfactory for making devices. It is not know how the crystal structure or surface morphology of the initial CdTe film contributes to the surface irregularities in the final HgCdTe sample; however, it is plausible that an improved substrate film will improve the final HgCdTe film properties.

3.1.2 Process Description

Pulsed electron beam processing was the technology proposed to smooth the film surfaces and to improve the crystal structure. A large diameter, low electron–energy beam is used to melt a thin surface layer of CdTe. Energy deposition is confined to the near surface region of the sample by the low particle energy. Thermal diffusion of energy away from this region is insignificant for the short duration (less than 0.1 microsecond) of the pulse. This, combined with the low total energy deposited in the film, typically less than 1 joule/cm^2, insures that only a thin layer of the sample is melted. The liquid cools quickly by heat conduction to the solid substrate. Epitaxial crystal growth and surface smoothing are observed. Spalling of the liquid and outdiffusion of an atomic species are minimized by the short duration of the melt phase.

For this phase of the program it was considered desirable to process the CdTe films although the feasibility of pulsed electron beam processing of HgCdTe for surface smoothing was shown in the first phase. Processing CdTe samples was considered desirable because the entire film thickness typically deposited by HWE could be melted by the pulsed electron beam for complete epitaxial growth from the substrate. Parameters for HgCdTe films are determined by device requirements, and these films are thicker than the layer which can be pulse melted and cooled in its entirety with minimal loss of stoichiometry. Pulsing the CdTe films is also desirable as the later EDICT process would insure stoichiometry of the surface.

3.1.3 Experimental Results

The results of pulsed polishing heteroepitaxial CdTe films were previously presented.[4] The new results shown here, (a) compare the effects of EDICT on pulsed material to pulsing HgCdTe directly, and (b) show that a 2-inch diameter sample can be processed (as called for by the statement of work).
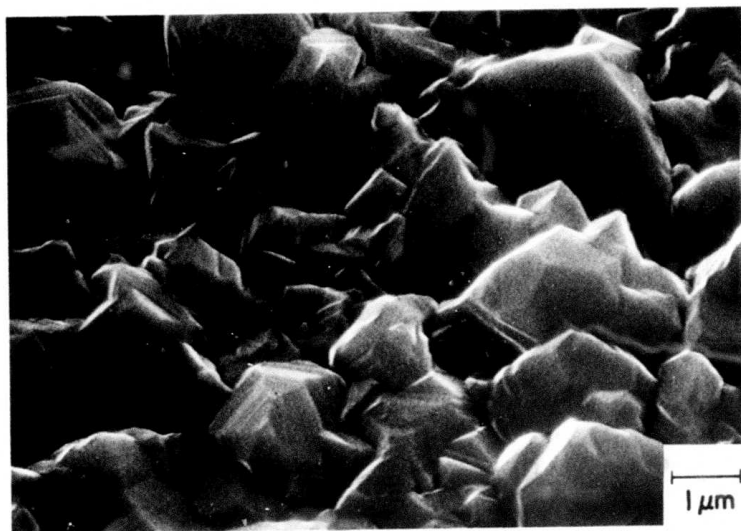
At the start of this program NERC used two samples for the EDICT process; M100H which was a CdTe film pulse polished in a limited area by Spire, and M132 which was a CdTe film of similar thickness and purity but never pulsed. The second sample, M132, was pulse processed in a limited area after EDICT. The results are shown in Figures 3-1, 3-2, and 3-3. In the first figure, the unpulsed (3-1a) and pulsed (3-1b) surface of the CdTe film M100H are shown. In the second figure, unpulsed (3-2a) and pulsed (3-2b) regions of the same sample M100H after EDICT are shown. There is no significant difference between the two regions. The film is a single crystal of HgCdTe with spiral terraces on the surface lined up with crystal orientation. The effect of pulsing these features is shown in Figure 3-3 where the growth terraces on sample M132 in (a) are reduced in size after melting as shown in (b). Optically, the films in Figures 3-1(b) and 3-3(b) are smooth and highly reflective, while the films in 3-1(a) and 3-3(a) are not.

The cause of the spiral growth terraces is not clear. NERC has shown that the highly irregular surface of the as-deposited CdTe films, composed of many small pyramids, is smoothed by the EDICT process. The size and structure of the terraces, however, are unrelated to that of the pyramids; and as shown by Figures 3-1 and 3-2, apparently unrelated to any surface morphology. EDS analyses of the two areas of sample M132 shown in Figures 3-2(a) and 3-2(b) are given in Table 3-1. The difference in composition between the pulsed and unpulsed areas after EDICT is not statistically significant. This evidence supports the contention that pulsed electron beam melting of the CdTe film does not affect the stoichiometry of the final HgCdTe film. The source of the silicon indicated in Table 3-1 is not known. It could be a surface contaminant or a bulk contaminant. In the latter case, silicon in such high concentration might have been responsible for the observed surface morphology.
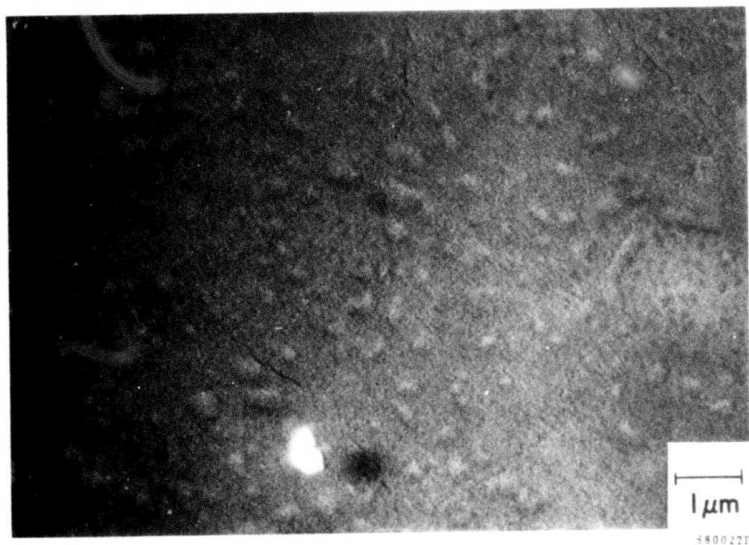
With additional development the tendancy to form the spiral growth terraces during the EDICT process was reduced (Section 2.2). However, no further conversions of pulse processed material were attempted.

TABLE 3-1.
STANDARDLESS EDS ANALYSIS OF SAMPLE M-100H.
HWE CdTe on mica converted to HgCdTe by EDICT.

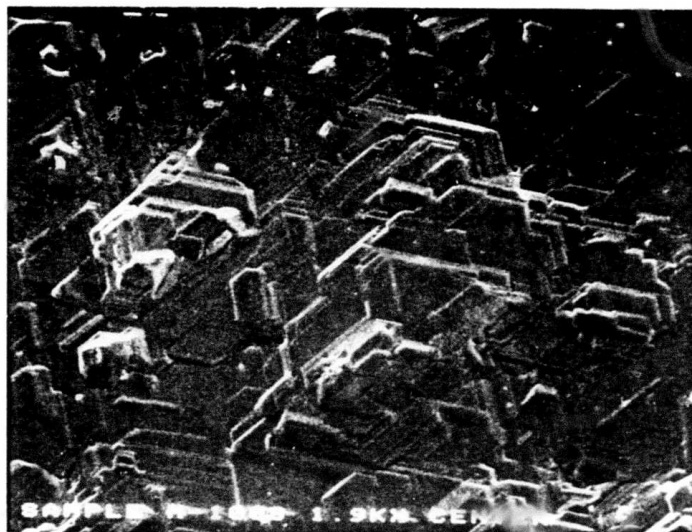| Element	Line	Atomic %	Precision 2σ
(Area not pulsed)			
Si	Kα	6.71	0.09
Cd	Lα	13.44	0.40
Te	Lα	53.08	1.20
Hg	Mα	26.78	0.76
(Area pulsed)			
Si	Kα	6.03	0.09
Cd	Lα	14.52	0.53
Te	Lα	53.66	1.28
Hg	Mα	25.79	0.80

(a) as-deposited

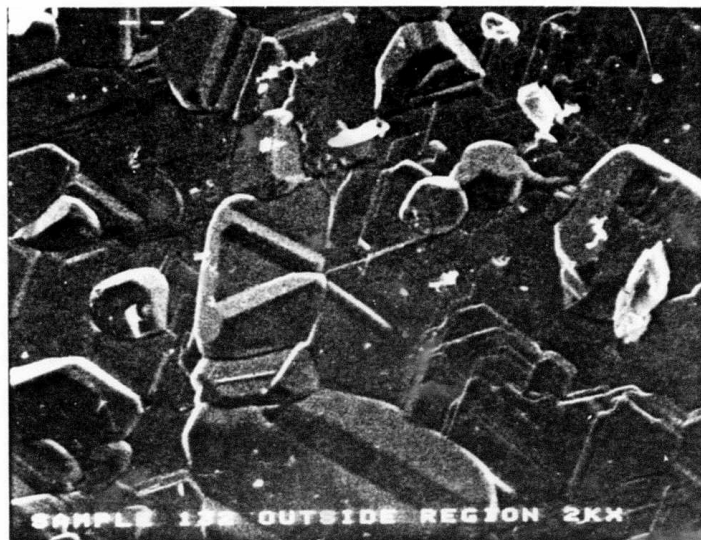(b) after pulse electron beam melting.

FIGURE 3-1.   HWE CdTe FILM ON MICA.

(a)

(b)

FIGURE 3-2. SEM MICROPHOTOGRAPH OF SAMPLE M-100H, HWE CdTe DEPOSITED ON MICA, (a) unpulsed and (b) pulsed regions then converted to $Hg_{.7}Cd_{.3}Te$ by EDICT.

(a)

(b)

FIGURE 3-3.   SEM MICROPHOTOGRAPH OF SAMPLE M132; HWE CdTe
DEPOSITED ON MICA AND CONVERTED TO HgCdTe by
EDICT. (a) Top, as-received, (b) Bottom, pulsed by
electron beam. (Second small line at upper left is one micron.)

A secondary amount of effort under this task was devoted to optimization of the electron beam parameters to obtain a uniform processing area 2 inches in diameter. This anticipated pulse processing of larger samples. At the end of phase one the region of CdTe pulse melted by an electron beam in one pulse was approximately 5x5 mm. This was extended to one inch diameter for processing of a film on an insulating substrate. No larger samples of this type were received. The uniformity of processing on a 3-inch diameter silicon wafer was measured as a test. In Figure 3-4 the sheet resistance of a wafer pulse electron beam annealed[5] with an implant of $\pm$1% uniform dose is shown. Excluding the edge, the variation in sheet resistance is between 30 and 38 ohms, with a standard deviation less than 10%. This was considered sufficient for this initial work, as it is not clear how sheet resistance relates to beam fluence or melt depth.

3.2   PULSED ELECTRON BEAM PROCESSING OF AMORPHOUS AND POLYCRYSTALLINE FILMS

3.2.1 Objective

This task had two distinct parts. The first objective was to demonstrate pulsed electron beam (PEB) liquid phase heteroepitaxy of HWE CdTe films on foreign substrates. Initial work in phase one of this program showed that CdTe films deposited on sapphire were polycrystalline. NERC believed that single crystal films could be obtained through changes in the HWE furnace alone. Spire believed that PEB processing was an essential alternate method of improving the crystal structure of the film.

The second objective was to demonstrate pulsed electron beam (PEB) liquid phase heteroepitaxy of evaporated films of HgTe on CdTe substrates. This completely different approach to forming thin HgCdTe films was to eventually use foreign substrates. The feasiblity of pulsing evaporated Hg films on cooled substrates was demonstrated in phase one of this program. Crystalline semiconductor films were sought in this phase.

3.2.2 Polycrystalline CdTe Films on Sapphire

Two CdTe films deposited on sapphire were received from NERC. Both were polycrystalline, about 1-3 cm^2. Sample 1080S was 2 microns thick and sample 1082S was a 7 micron thick film. The thinner sample was considered to be in the proper thickness range for pulsed melting of the entire film.

SPIRE   ARSENIC   RS

WAFER NO.   2055-6

AVERAGE R(SHEET)=34.5 OHMS/SQUARE

STD. DEV. = +/-3.73   RANGE =+/- 7.45 OHMS/SQUARE

IMPLANT CONDITIONS-

TILT= 7   ENERGY= 25KEV   FLUENCE = $5 \times 10^{15}/cm^2$

                                    ANNEAL SPEC- PEBA 280

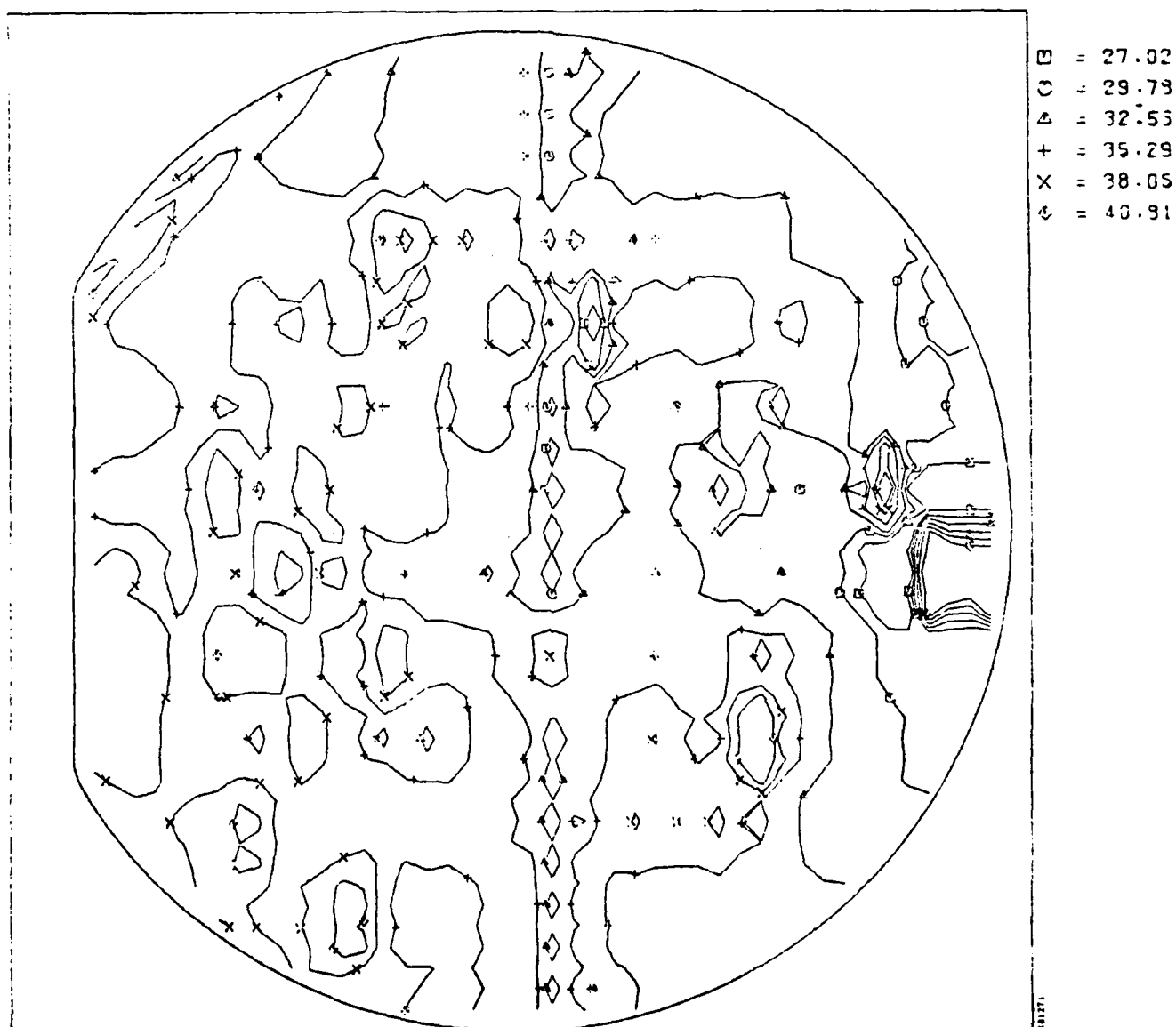|	
⊡	= 27.02
○	= 29.78
△	= 32.53
+	= 35.29
✕	= 38.05
◇	= 40.91

FIGURE 3-4   SHEET RESISTANCE OF 3-INCH DIAMETER
              SILICON WAFER, ION IMPLANTED AND ANNEALED
              BY PEBA.

The samples were mounted and examined in an SEM using electron channeling techniques to search for information on crystal structure. No channeling pattern could be detected from the pulsed area or the as-deposited film. In the last case this implied that the film was fine grained polycrystalline material with random orientation. For the pulsed area, the lack of a channeling pattern implies that either heteroepitaxial growth did not occur at all (and the film remained fine grained polycrystalline material) or that the surface of the film is heavily damaged if it is crystalline. Since previous work with PEB liquid epitaxy on silicon produced films with excellent electron channeling and diffraction patterns,[6] the lack of such a pattern implies no epitaxial growth.

The samples in the SEM were also examined using RBEI (Robinson Backscattered Electron Imaging).[7] This technique enhances the contrast between different elemental compositions in an otherwise uniform surface film. The results are shown in Figure 3-5. The thinner sample in (b), 1080S, has been completely melted. Before freezing the surface became irregular with parts of the substrate showing black through holes in the film. Fine cracks running between these holes cover the surface. The thicker sample in Figure 3-5(c) has wider cracks but no holes. Irregular surface features are still apparent but none has penetrated to the substrate and a more uniform contrast is seen. These pictures can be compared to Figure 3-5(a), the as-deposited film, which has a highly irregular fine grain morphology. Optically, the film in (a) appears dark grey and non-reflective while the films in (b) and (c) have a bright, silvery reflective appearance.

At this time, there is no clear explanation for the lack of success in PEB liquid phase heteroepitaxy. One possible explanation is contamination on the substrate surface prior to deposition of the CdTe. This would have prevented epitaxial growth in HWE as well as PEB processing unless the contaminant would dissolve in molten CdTe.
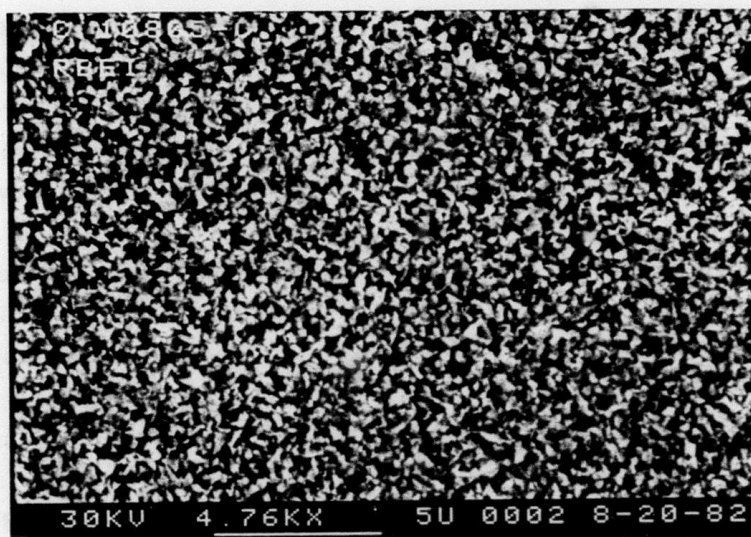
FIGURE 3-5(a). SEM MICROGRAPH OF CdTe FILM DEPOSITED ON
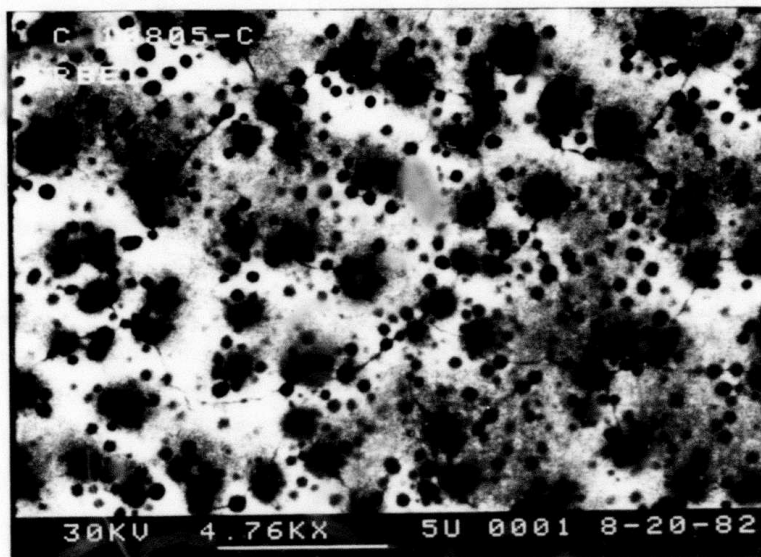SAPPHIRE BY HWE, 2 MICRONS THICK.

FIGURE 3-5(b). SEM MICROGRAPH OF PULSED (0.30 J/cm2) CdTe
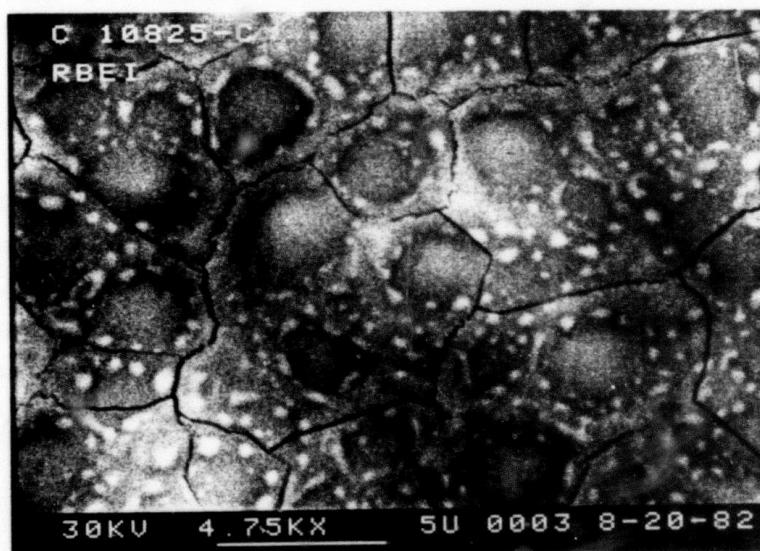FILM ON SAPPHIRE, 2 MICRONS THICK.

FIGURE 3-5(c). SEM MICROGRAPH OF PULSED (0.35 J/cm2) CdTe
FILM ON SAPPHIRE, 7 MICRONS THICK.

3.2.3 Evaporated HgTe on CdTe

The purpose of the work was to show that a crystal substrate could be cleaned by PEB processing in vacuum, have a Hg and Te film co-evaporated onto its surface, and then show epitaxial growth of the film by PEB processing. It was considered desirable to perform all of these steps in one vacuum chamber to maintain clean surfaces. It was also believed necessary to cool the evaporation target for Hg condensation; even though Hg and Te were co-evaporated it was not known if Hg would be bound to the surface in stoichiometric concentrations at room temperatures.

The equipment built for this experiment is shown schematically in Figure 3-6. The sample is mounted on a liquid nitrogen cooled can at the center of the vacuum chamber. It can be rotated 360°. The pulsed electron beam source (diode and guide cone) is mounted at one end of the chamber, and the evaporation furnaces are mounted at the other end. An optical port for observing the sample is on one side. As configured, the chamber is pumped through the electron beam diode, but a 4-inch diffusion pump stack can be mounted on the bottom of the chamber if lower pressures are needed. The furnace for the mercury vapor source is mounted outside of the vacuum system. Initial work has shown that the vapor pressure of Hg near room temperature is sufficient for evaporation. The tellurium source furnace is heated by resistance wire and monitored by a thermocouple; temperatures near melt (450^OC) are required.

At the time the contract was terminated, the first series of calibration runs for checking deposition rates onto hot (300^OK) and cold (77^OK) substrates were run. Also, initial measurements of the fluence delivered by the electron beam source to the sample had been taken. One single-crystal CdTe wafer had had a surface coating applied and been pulsed. Neither the deposit nor the pulse processed material was crystalline. The substrate was damaged at a fluence of 0.25 J/cm^2 (slip lines) but not at 0.22 J/cm^2. No further work with this apparatus was attempted after contract termination.
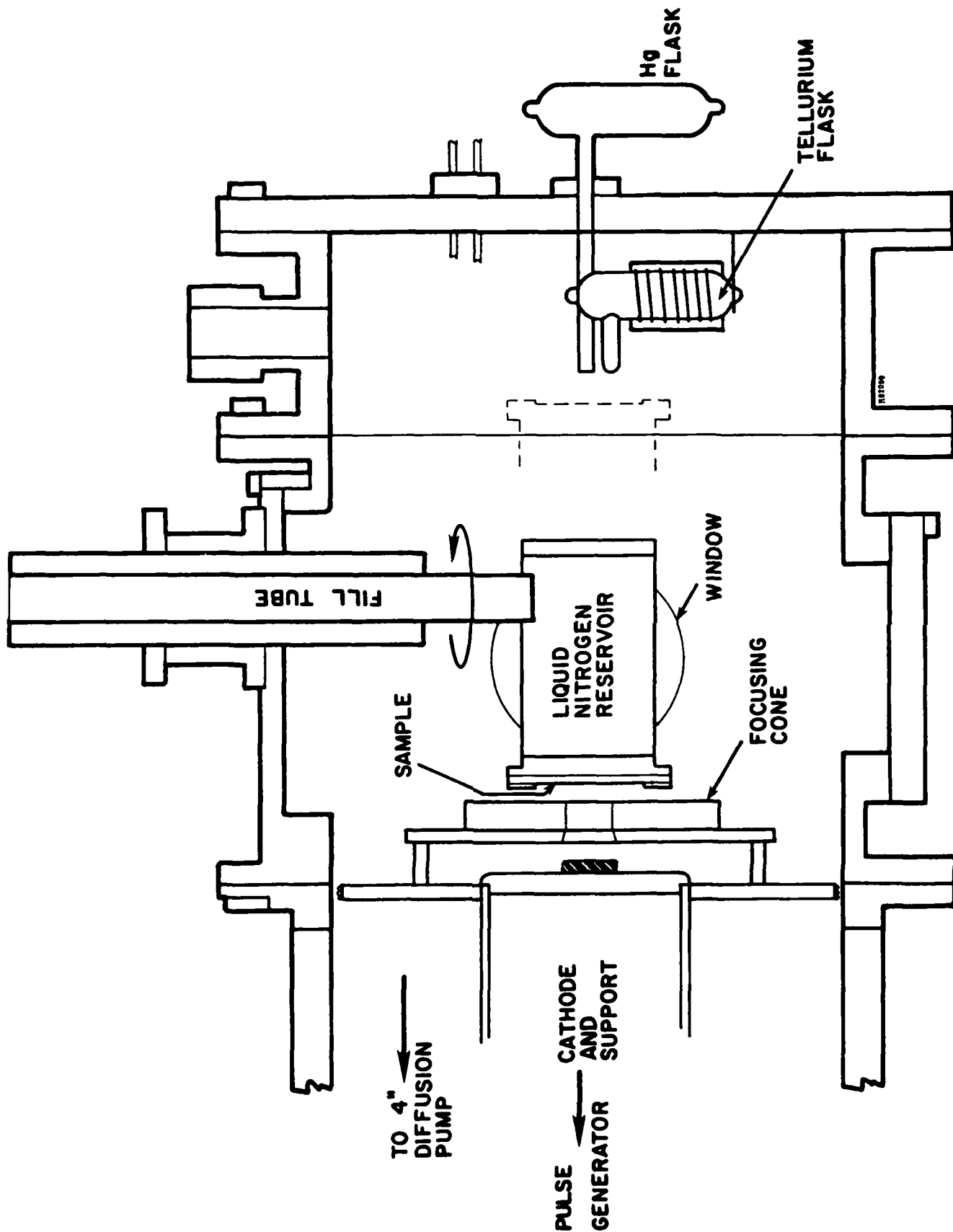
FIGURE 3-6. SCHEMATIC DIAGRAM FOR EVAPORATION OF Hg AND Te, AND PULSED ELECTRON BEAM IRRADIATION IN SITU.

SECTION 4
CONCLUSIONS

4.1 ACCOMPLISHMENTS

At the termination of this contract, the following results had been shown:

For HgCdTe films on mica:

- One inch diameter (111) single-crystal films.
- 8 to 14 micron thick films grown by HWE at 7 to 12 microns per hour.
- Substrate and source temperatures varied from 380 to 525°C.
- Growth rate increased with increasing substrate temperature.
- Growth rate apparently controlled by diffusion.
- CdTe successfully converted to single crystal $Hg_{1-x}Cd_xTe$ (x~0.3) at 500°C.
- Surface morphology and crystal structure improved by EDICT.

For HgCdTe films on sapphire:

- Two inch diameter films were grown on variously oriented sapphire.
- All films were polycrystalline, up to 180 microns thick.
- Deposition rates (minimum 10 microns/hour) increased with increasing substrate temperature over the range 325 to 490°C.
- Rate controlling step may be bond formation.
- Thin films were mirror-like, coarseness increases with film thickness.
- Coarseness was the only variable which seemed to be orientation dependant.
- CdTe films converted to $Hg_{1-x}Cd_xTe$ by EDICT at 500°C for 72 hours.
- Values of x between 0.2 and 0.3 were obtained.

For pulsed electron beam processing:

- CdTe films, 2 to 14 microns thick, up to one inch diameter, on mica and sapphire were irradiated at different fluences 0.1 to 1.0 J/cm^2.
- HgCdTe films on mica were irradiated at different fluences 0.1 to 1.0 J/cm^2.
- Liquid phase heteroepitaxial crystal growth was not observed in either case.
- Films were single-crystal if so initially, and if not melted completely.
- Surface polishing of HgCdTe is feasible.
- Loss of stoichiometry was minimal.
- The surface morphology of the CdTe films on mica did not affect the microscopic surface features seen after EDICT.

SECTION 5
REFERENCES

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